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Effect of annealing on photovoltaic characteristics of nanostructured $p-Cu_2S/n-CdS$ thin film

Vidya S. Taur^a, Rajesh A. Joshi^a, Anil V. Ghule^b, Ramphal Sharma^{a,*}

^a Thin Film and Nanotechnology Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India ^b Department of Nanotechnology, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India

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ABSTRACT

Nanostructured heterojunction solar cells of CdS/Cu₂S were grown by simple chemical ion exchange reaction by immersing the CdS thin films in Cu ion solution at room temperature. The as-grown nanostructured thin films were annealed at 250 °C in air for improving the interface and crystallinity of the heterojunction. These as grown and annealed nanostructured heterojunction were characterized for photovoltaic and other optoelectronic characteristics. Increase in conversion efficiency is obtained from annealed ($\eta = 0.24\%$) than the as grown heterojunction ($\eta = 0.09\%$), on illuminating to 100 mW/cm² light source. The X-ray diffraction (XRD) pattern confirms improvement in crystallinity with increase in crystallite size from 29 to 32 nm on annealing. The optical absorbance strength observed to be increased along with red shift in energy band gap value from $E_{\rm g} = 2.02-2.20$ eV after annealing.

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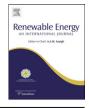
1. Introduction

Nanostructured heterojunction are the subject of active research for many optoelectronic devices such as semiconductors, LASER, photo detectors, solar cells etc. [1,2]. Among them the heterostructures of n-CdS/p-Cu₂S is most extensively studies for photovoltaic applications where the nanostructured n-CdS is one of the material used in solar cells as window material because of its high absorption coefficient and wide energy band gap $E_g = 2.42$ eV [3]. Use of Cu₂S as an absorber material in photovoltaic applications has the cause of its potential properties such as elemental abundance, p-type nature, high optical absorption coefficient in the visible part of solar spectrum ($\alpha > 10^4$ cm⁻¹), bulk energy band gap 1.21 eV and environmental stability. So it has been explored in optoelectronic devices with special interest in photovoltaic applications in combination with CdS [4].

The conversion efficiency achieved till date in such nanostructured heterojunction photovoltaic modules, which are prepared using various physical and chemical techniques like vacuum evaporation, sputtering, spray pyrolysis, electro-deposition, chemical bath deposition [5–8] etc. has some limitations induced by poor stoichiometry, surface and interface between the window and absorber layer. These problems can be sorted out by using the ion exchange method at room temperature for heterojunction synthesis. In literature the chemical ion exchange method described as one of the easiest, user friendly and desired interface forming method. During the ion exchange method, replacement of anion sub-lattice provides the partial conversions of the surface nano-crystals to create a heterostructures, where the two compounds such as window and absorber layers share a common anion [9]. Even the interface formed by this ion exchange method can be further modified using post deposition treatment such as annealing [10,11]. In literature abundant research reports are available about providing the annealing treatment for improving the conversion efficiency, through modifications in crystallinity and interface [12–15] but rarely there may be any report available on use of annealing treatment for improving the conversion efficiency in CdS/Cu₂S heterojunction.

Hence here in the present study we report on interface modification by following the chemical ion exchange method for synthesis of n-CdS/p-Cu₂S heterojunction in which the cation Cd from CdS get partially replaced by Cu ion originating from CuSO₄ solution to form homogenous CdS/Cu₂S interface [16,17] and study the annealing effect at 250 °C on conversion efficiency of these nanoheterojunctions [18]. The obtained as grown and annealed CdS/Cu₂S interface heterojunction were characterized for photovoltaic characteristics by illuminating to 100 mW/cm² light source. The structural and elemental electronic characterizations by XRD and XPS techniques, surface morphology analyzed by atomic force microscopy images (AFM) obtained from as grown and annealed heterojunction respectively. The optical properties





^{*} Corresponding author. Tel.: +91 9422793173, +91 240 2401365; fax: +91 240 2403115/2403335.

E-mail addresses: rps.phy@gmail.com, ramphalsharma@yahoo.com (R. Sharma).

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such as absorbance strength and energy band gap by UV-Vis spectrophotometer.

2. Experimental

2.1. Synthesis method

The window layer of CdS thin films synthesized onto ITO coated conducting glass substrates by using simple chemical bath depositions (CBD) technique with deposition temperature maintained at 80 °C using cadmium sulfate (CdSO₄) and thiourea (SC(NH₂)₂) as source of Cd and S respectively. The growth mechanism involved in the formation of CdS includes reaction between the cationic and anionic solution in an alkaline medium with deposition rate as a function of reaction bath temperature. The aqueous solutions of two reactants were mixed, while pH was set at 11 the reaction carried for 1 h to obtain yellowish-orange colored nanostructured CdS thin film. The mechanism of CdS formation can be shown as follows.

$$Cd^{2+} + 4NH_3^+ \rightarrow Cd(NH_3)_4^{2+}$$
 (1)

$$Cd(NH_3)_4^{2+} + S^{2-} \rightarrow CdS \downarrow + 4NH_3 \uparrow$$
(2)

Such films were then used for growth of Cu₂S layer by ion exchange method using CuCl as the source of Cu ion this can be achieved by immersing the CdS thin films in Cu solution for fix interval of time. As the ion exchange reaction is time dependent phenomenon so if the immersion time increased then there may be lot of possibilities for total conversion of surface layer CdS to Cu₂S. The Cu₂S phase formation confirmed by gray color appearing at the surface. The reaction mechanism followed during ion exchange would be as follows,

$$CdS + 2CuCl \rightarrow Cu_2S + CdCl_2$$
(3)

The as grown CdS/Cu₂S nanostructured heterojunction were annealed at 250 °C in air to improve the crystallinity and resultant interface [18]. These as grown and annealed heterojunction of nanostructured CdS/Cu₂S characterized for photovoltaic, structural, compositional and optical properties.

2.2. Characterization

The structural properties observed from the X-ray diffraction (XRD) pattern obtained on Bruker, AXS, Germany (D8 Advanced)

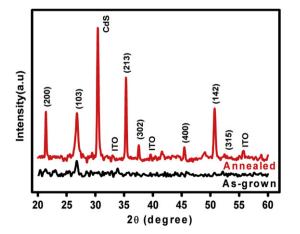


Fig. 1. XRD pattern of as grown and annealed nanostructured n-CdS/p-Cu₂S heterojunction synthesized by the simple chemical ion exchange method at room temperature.

diffractometer in scanning range $20-60^{\circ}$ (2θ) using CuK α radiation with wavelength 1.5406 Å. Chemical composition analyzed by studying X-ray photoelectron spectroscopy (XPS) measurements using VG Multi Lab ESCA 2000 system. The surface morphology of the heterojunction probed by using atomic force microscope (AFM) images monitored on Nanoscope III from Veeco digital instrument. The optical characterization performed with the help of UV–Vis

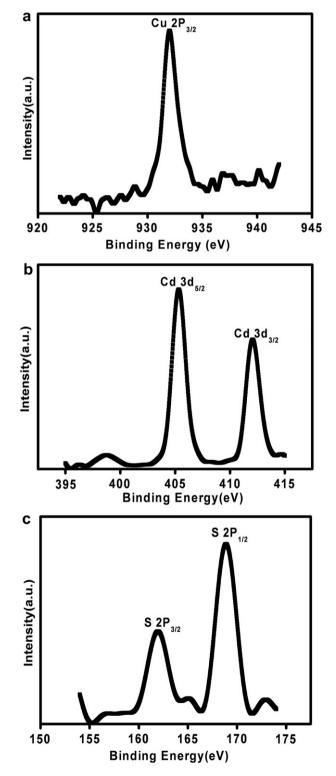


Fig. 2. XPS spectra of n-CdS/p-Cu₂S used for chemical composition analysis (a) S 2p, (b) Cd 3d and (c) Cu 2p.

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