Applied Surface Science 255 (2009) 6115–6120

Contents lists available at ScienceDirect

Applied Surface Science

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

# Structural, optical and photoelectrochemical characterization of CdS nanowire synthesized by chemical bath deposition and wet chemical etching

J.K. Dongre *, Vikas Nogriya, M. Ramrakhiani

*Dept. of Postgraduate Studies and Research in Physics & Electronics, Rani Durgawati University, Pachpedi, Jabalpur (M.P.) 482001, India*

ARTICLE INFO

*Article history:*
Received 8 September 2008
Received in revised form 20 January 2009
Accepted 20 January 2009
Available online 30 January 2009

*PACS:*
81.16.Be
62.23.Hj
81.65.Cf
82.47.Jk

*Keywords:*
Chemical bath deposited CdS
Nanoparticles and nanowires
XRD
Surface morphology
Optical property
Photoelectrochemical cells

ABSTRACT

Nanocrystalline thin films of CdS have been grown onto flexible plastic and titanium substrates by a simple and environmentally benign chemical bath deposition (CBD) method at room temperature. The films consist of clusters of CdS nanoparticles. The clusters of CdS nanoparticles in the films were successfully converted into nanowire (NW) networks using chemical etching process. The possible mechanism of the etching phenomenon is discussed. These films were examined for their structural, surface morphological and optical properties by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and UV–vis spectrophotometry techniques, respectively. Photoelectrochemical (PEC) investigations were carried out using cell configuration as n-CdS/(1 M NaOH + 1 M $Na_2S$ + 1 M S)/C. The film of nanowires was found to be hexagonal in structure with the preferential orientation along the (0 0 2) plane. The nanowires have widths in the range of 50–150 nm and have lengths of the order of a few micrometers. Optical studies reveal that the CdS nanowires have value of band gap 2.48 eV, whereas it is 2.58 eV for nanoparticles of CdS. Finally, we report on the ideality of junction improvement of PEC cells when CdS nanoparticles photoelectrode converted into nanowires photoelectrode.



## 1. Introduction

One-dimensional (1D) semiconductor nanostructures have drawn intensive interest due to their fundamental research and potential applications in fabrication of nanoscale devices. CdS, one of the very important II–VI group semiconductors, plays an important role in optoelectronic devices such as lasers, light-emitting diodes and solar cells. In recent years, considerable efforts have been made to synthesize CdS nanostructures by several methods such as electrochemical synthesis [1,2], chemical synthesis [3], solvothermal route [4], thermal evaporation [5], chemical vapor deposition [6], vapor–liquid–solid growth [7] etc.

One way to make a nanowire (NW) is etching (dry and wet) process, by which variety of materials such as GaAs, Si, and rhenium [8–11] has been fabricated. Beside this, several approaches have been used for nanowire fabrication using chemical etching technique. Ling-min et al. [12] have synthesized $CdS/SiO_2$ nanowire arrays and CdS nanobelts by thermal evaporation of mixture of CdS and CdO powders with highly selective etching occurring on the silicon substrate surfaces. Maynor et al. [13] have created unique diameter-modulated GaN nanowires by reacting the wires of different diameters with 1 M hydrochloric acid (HCl). Using seed-mediated growth approach Sajanlal and Pradeep [14] have converted gold nanoparticle into nanowire and nanoplate at certain cetyltrimethylammonium bromide (CTAB) concentration in the presence of ascorbic acid. Kim et al. [15] have also reported that silver nanorods and nanowires can be successfully synthesized by converting nanoparticles at a relatively low temperature of 50 °C. Recently, Zhang et al. [16] have prepared CdS nanowire by chemical bath deposition (CBD) using porous anodic aluminium oxide (AAO) template.

In this paper, we report the synthesis of film of CdS nanowire by a simple chemical bath deposition process followed by chemical etching, which is an easier, low-cost and highly efficient technique. Most of the synthetic processes reported previously required suitable capping agents or stabilizing agents or nano-order poring system such as porous aluminium oxide etc. for synthesis of nanostructured materials. In this work we have not used any capping agents/stabilizing agents or surfactants for synthesizing nanomaterials.

* Corresponding author. Tel.: +91 761 2340707.
*E-mail addresses:* jk_dongre@yahoo.com (J.K. Dongre), mramrakhiani@hotmail.com (M. Ramrakhiani).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.01.064

## 2. Experimental details

### 2.1. Preparation of CdS films

In the present study analytical grade reagents were used without any further purification. Preparation method of CdS nanostructures consisted of two steps. In the first step films of CdS nanoparticle were prepared by CBD. The nanoparticle films were converted into fibril-like nanowire using chemical etching in second step.

CdS film of nanocrystallites was prepared by CBD technique [17], on transparent plastic sheet and titanium (Ti) substrates. Initially, the substrates were washed with double distilled water and etched in dilute hydrochloric acid for few second. Again, the substrates were washed with detergent, rinsed in acetone and finally ultrasonically cleaned with double distilled water before deposition of thin film.

For deposition of CdS nanocrystallites 1 M $CdSO_4$ solution was prepared in 10 ml of double distilled water, and then 1.9 M $NH_4OH$ solution was added to it till it becomes completely transparent. This clear solution was kept under unstirred condition and substrates were dipped in it for a few hours. Whitish films were formed on transparent plastic sheet and Ti substrates. The above clear solution was freshly prepared again and to this transparent solution of $CdSO_4$ + $NH_4OH$, 10 ml of 1 M thiourea solution was added. As prepared whitish film coated substrates fixed to the substrates holder were dipped in the solution and rotated continuously by a motor (∼125 rpm). Nanocrystalline sample was prepared from an aqueous alkaline bath (pH ∼ 12) with deposition time 5 h, at room temperature 300 K. These CdS films were washed with a fine water jet to remove surface adsorbed particles and then dried in air for 2 days.

For chemical etching vessel containing freshly prepared 0.1 M of hydrochloric acid solution was kept inside an ice bath throughout the process. The freshly prepared layer of nanoparticle coated substrate was immediately immersed in above solution for 5 s. After completion of chemical etching, the substrate was taken out, washed using double distilled water in order to remove the HCl from the substrate and allowed to dry in air before characterization.

The thickness of CdS film was measured with the help of weight difference method employing sensitive electronic microbalance. Thickness of film was 434.68 nm. The structural characterization of CdS nanowires film was performed by an X-ray diffractometer (Rigaku rotating anode H-3R) using Cu Kα radiation taken from 10° to 60°. The surface morphology of the film was characterized by scanning electron microscopy (SEM; JEOL-JSM 5600) and atomic force microscopy (AFM; DIAFM-4). The transmission data in the range 400–700 nm were obtained with PerkinElmer, Lambda-35 spectrometer. Photoelectrochemical (PEC) cell was fabricated using a two electrode configuration, comprising n-CdS thin film as photoelectrode and graphite as a counter electrode. The redox electrolyte was an aqueous solution of 1 M NaOH + 1 M $Na_2S$ + 1 M S. The distance between working electrode and counter electrode was fixed to 10 mm with plastic cello-tape spacer. Photocurrent–voltage (I–V) performances of as-deposited and etched CdS photoelectrodes were measured under 100 mW/cm$^2$ light illumination intensity.

## 3. Results and discussion

### 3.1. X-ray diffraction studies

The crystallinity of the prepared CdS nanowire sample was investigated by X-ray diffraction (XRD). As shown in Fig. 1 the most intense peak at $2\theta = 26.12°$ can be attributed to (0 0 2) hexagonal

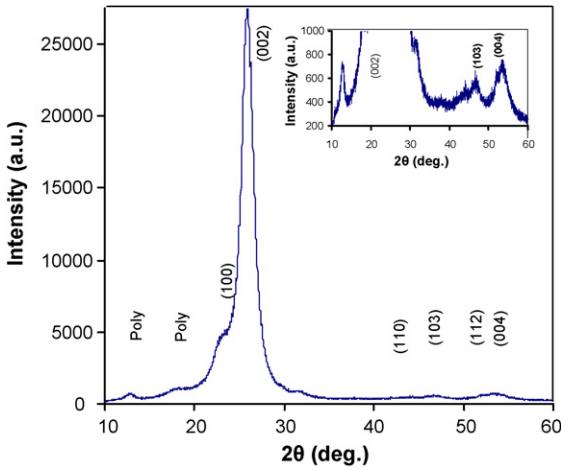


**Fig. 1.** X-ray diffraction pattern of CdS nanowires film formed on flexible plastic substrate. Inset shows broadening of most prominent peaks of hexagonal CdS at low intensity and values of $\beta$ is calculated from these peaks.

(H) or (1 1 1) cubic (C). Similarly the peak at 53.78° can be indexed as (0 0 4) H or (2 2 2) C. But the peaks at 24.14, 47.4 and 51.94 purely correspond to (1 0 0), (1 0 3) and (1 1 2) planes of hexagonal CdS, respectively [18]. However, two additional peaks at an angle of 13° and 18.64° are due to crystalline nature of plastic [19]. Plastic is well known as a crystalline polymer. So we can conclude that the nanowire film predominantly has a wurtzite hexagonal structure with a preferential orientation along the (0 0 2) plane. This indicates that the nanowire networks are parallel to plastic substrate [20]. The several weak diffraction peaks may come from some randomly oriented CdS NWs. Similar results have been observed by Acharya et al. [21], by pulsed-laser deposition and Perna and Capozzi [22], by laser ablation technique. The lattice constant $c$ (along the $c$-axis) and the lattice constant, $a$, can be determined from the interplanar spacing of different ($h\,k\,l$) planes using the method suggested by Runyan and Watelski [23]:

$$(d_{hkl})^{-2} = 4\frac{\left(h^2 + hk + k^2\right)}{3a^2} + \left(\frac{l}{c}\right)^2. \quad (1)$$

The lattice constant $c$ = 6.801 Å was obtained from the $d$-value of H (0 0 2) peak. Also $c$ = 6.7436 Å was obtained from the $d$-value of H (1 0 3) and H (1 0 0) peaks according to relation $c^{-2} = (d_{1\,0\,3})^{-2} - (d_{1\,0\,0})^{-2}/9$, which was deduced from (1). The average of these two values is calculated as $c$ = 6.7723 Å. Taking the $c$-value obtained from the H (0 0 2) peak and the $d$-values of other diffraction peaks and using (1), several values were obtained for the lattice constant $a$. These data are plotted against $F(\theta) = \cos^2\theta/\sin\theta + \cos^2\theta/\theta$ in Fig. 2. This is a method by which the effect of random and systematic errors on the measurement of $\theta$ is minimized and the precise value of the lattice constant is obtainable from the vertical intercept of the straight-line fit [24]. The vertical intercept of the fitted line yields $a$ = 4.1409 Å. These values of lattice constant $c$ and $a$ estimated by our experiment are nearly same as reported in the literature [25].

The X-ray diffraction pattern of CdS nanowire on flexible plastic substrate shows a broadening of the peaks, which indicate that CdS is nanocrystalline in nature. Peak broadening may be caused by residual stresses and grain size that may be present in the wire; hence Scherrer's equation may produce results that are different from the actual size [26]. Stresses within the crystal cause corresponding strains, which result in a change of planar spacing and shifting the peaks. Often residual stresses produce a combination of compressive and tensile strains. In order to