Journal of Crystal Growth 377 (2013) 112–117

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

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

Facile fabrication of CdS nanorod arrays on the transparent conducting substrates and their photoelectrochemical properties

Meiling Sun, Wuyou Fu, Qian Li, Guangchao Yin, Kailin Chi, Xiaoming Zhou, Jinwen Ma, Lihua Yang, Yannan Mu, Yanli Chen, Haibin Yang*

State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, China

ARTICLE INFO

Article history:
Received 12 April 2013
Received in revised form
8 May 2013
Accepted 13 May 2013
Communicated by K. Deppert
Available online 20 May 2013

Keywords:
A1. Nanostructure
A1. Optical properties
A2. Hydrothermal crystal growth
A3. Chemical bath deposition
B1. Cadmium compound
B2. Semiconducting II–VI materials

ABSTRACT

Oriented and high-density CdS nanorod arrays were successfully grown on transparent conductive substrates by facile chemical bath deposition and hydrothermal method free from organic solvents and surfactants. The morphology, structure and phase composition of these samples were examined, and the results demonstrated that the high purity and uniform single crystal hexagonal CdS nanorod array was obtained. Further investigation revealed that chemical bath deposition time played an important role in the formation of high quality CdS nanorod array. In addition, the optical absorption spectra and photoelectrochemical properties were also studied. It was found that the CdS nanorod film demonstrated superior photoelectrochemical properties when the chemical bath deposition and hydrothermal time were 30 min and 14 h respectively, which was ascribed to the large absorption coefficient of the material and the excellent charge collection efficiency of the nanorods. These results demonstrated that the CdS nanorod film had a potential application in various nanostructured optoelectronic devices.

1. Introduction

One-dimensional (1D) nanostructures such as nanowires, nanorods and nanotubes have gained considerable attention owing to the significance of these structures and the potential for developing nanodevices [1,2]. These 1D nanostructures provide unique electronic, optical and mechanical properties [3–5]. Moreover, they improve reaction activity because of quantum size effects, surface reconstruction and surface curvature, which thus make the system more effective and even allow for entirely novel reaction pathways [6,7]. Therefore, 1D nanostructures have potential applications in next generation devices, functional materials and sensors [8,9]. Particularly, 1D inorganic semiconductor arrays are considered as effective inorganic candidates to improve the efficiency of photovoltaic solar cells due to the efficient charge transport and large surface area [10–12].

As an important II–VI semiconductor, CdS has been known as one of the most promising photo-sensitive materials due to its unique photochemical activities and strong visible-light absorption [13–15]. It is a well-studied semiconductor with a direct band gap of 2.4 eV at room temperature and large absorption coefficient of $4\times10^4\ \text{cm}^{-1}$ [16]. Therefore, it is attractive material for application in photovoltaic solar cells, nonlinear optical devices, flat panel displays, light-emitting diodes, lasers, transistors and so on [17–20]. Over the past few years, tremendous efforts have been made to control the size and shape of CdS nanocrystals, and various methods have been reported for the synthesis of 1D CdS nanostructures such as metal-organic chemical vapor deposition method [21], thermal evaporation method [22,23], catalyst-assisted vapor–liquid–solid synthesis [24], laser-assisted catalytic growth [25], and electrochemical deposition process [26]. However, compared to the synthesis of TiO_2, ZnO, and CdSe nanomaterials for photovoltaic solar cells, the fabrication of CdS nanomaterials is still in a preliminary stage. Generally, the preparation methods involve rigorous experimental conditions, complex procedures, sophisticated equipment, and relatively high cost. Consequently, it is important to develop a facile method to synthesize 1D CdS array.

In this study, we described a facile and inexpensive approach for large-scale synthesis of oriented and high-density CdS nanorod (NR) arrays on fluorine-doped tin dioxide (FTO) glass substrates by chemical bath deposition (CBD) and hydrothermal method free from organic solvents and surfactants. The reaction conditions and characterization of the CdS NR films were discussed. The CdS NR film demonstrated superior photoelectrochemical (PEC) properties, which was ascribed to the large absorption coefficient of the material and the excellent charge collection efficiency of the nanorods. These results demonstrated that the CdS NR film had a potential application in various nanostructured optoelectronic devices.

---

* Corresponding author. Tel./fax: +86 431 85168763.
E-mail address: yanghb@jlu.edu.cn (H. Yang).

0022-0248/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jcrysgro.2013.05.013

2. Experimental

All chemicals were in analytical grade and used as received without any further purification. In a typical synthesis, FTO substrates were ultrasonically cleaned sequentially in acetone, isopropanol, and ethanol for 15 min each and were finally dried with nitrogen gas. Before the hydrothermal experiment, a compact CdS layer was deposited onto the well-cleaned FTO substrate by CBD method. Typically, 0.02 M $CdCl_2 \bullet 2.5H_2O$ dissolved in 20 mL deionized water was added to 20 mL of KOH (0.5 M) to form a mixture. Then, 20 mL of NH_4NO_3 (1.5 M) and 20 mL of CH_4N_2S (0.2 M) were added to the mixture to give a clear solution. Afterwards, the clear solution was continuously stirred for about 30 min. Finally, the well-cleaned FTO substrate was vertically immersed into the clear solution. The deposition was carried out at 80 °C for 0–60 min and the FTO substrate was kept vertically in the bath. After this process, the film was cleaned with ethanol in an ultrasound bath for 30 s, and then rinsed with deionized water.

After coating the FTO substrates with compact CdS films, hydrothermal growth of CdS NRs arrays was achieved by suspending these substrates vertically to the bottom of the Teflon liner filled with 80 mL aqueous solution of 1 mmol of cadmium nitrate $Cd(NO_3)_2 \bullet 4H_2O$ and 3 mmol of thiourea. The hydrothermal synthesis was conducted at 210 °C for 14 h in an electric oven. After synthesis, the reaction solution was cooled to room temperature naturally. The sample was rinsed with deionized water and ethanol, and then dried under high-purity nitrogen flow. After this process, the as-prepared samples were immersed in saturated cadmium chloride methanol solution for 10 seconds and subsequently annealed at 400 °C for 20 min in N_2 atmosphere [27].

A model JEOL JSM-6700 F field emission scanning electron microscopy (FESEM) was used to characterize the morphologies of the samples. The crystal structures were identified by X-ray diffractometer (XRD, Rigaku D/max-2500) with CuKα radiation ($\lambda = 1.5418$ A). Energy dispersive X-ray analysis (EDX) of the CdS NR array was performed with an EDAX Genesis 2000 system (FEI Inc) installed on the XL 30 ESEM imaging instrument. The transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) pattern were taken on a JEOL JEM-2200FS with an accelerating voltage of 200 kV. A UV-3150 double-beam spectrophotometer was used to characterize the optical absorption spectra. The CdS NR electrodes were incorporated into thin-layer sandwich-type cells with Pt as the counter electrodes and electrolyte solutions to measure the PEC properties. A mixture of 0.25 M Na_2S and 0.35 M Na_2SO_3 aqueous solution was used as the electrolyte. A 500 W xenon lamp was used as a light source and its light intensity was adjusted to simulate AM 1.5 at 100 mW cm^{-2} with a laser power meter (BG26M92C, Midwest Group). The active area was strictly kept within 1 cm^2 by coating a layer of waterproof rubberized fabric on the excess area.

3. Results and discussion

3.1. Characterization of CdS nanorod arrays

Fig. 1a–e shows the FESEM images of CdS NR arrays prepared for different CBD time (0, 15, 30, 45 and 60 min, respectively) and the same hydrothermal time (14 h). It is obvious from Fig. 1a that the low-density CdS NRs appear less aligned with the substrate surface normal and part of the FTO is exposed to air. As shown in Fig. 1b–e, the entire surface of the FTO substrate is covered uniformly and densely with CdS NRs. The NRs are hexangular in shape, the expected growth habit for the hexangular crystal structure. It is clear that the density of the NRs could be varied between ~50 to ~85 wires μm^{-2} and the length of the NRs were from 300–600 nm to 100–250 nm by increasing the CBD time from 0 min to 60 min. This appearance might be a result of the changing CdS nanoparticle (NP) density. When CdS NP density is high, the high-density NRs run into neighboring nanorods and stop growing [28]. On the other hand, when CdS NP density is low, the low-density NRs can keep growing to longer lengths since the probability of running into a neighbor decreases [28]. For comparative study, the pure CdS NP film (250 nm in thickness) in Fig. 1f was also prepared by the same CBD method for a longer reaction time (2 h).

The phase structure and chemistry composition of the samples were examined by XRD and EDX. Fig. 2 displays the XRD patterns of the CdS films prepared for different CBD reaction time and hydrothermal time. After being annealed at 400 °C for 20 min in a high-purity nitrogen atmosphere, the XRD data show an excellent agreement with the standard hexagonal wurtzite structure of CdS (JCPDS 41-1049). The strong and sharp diffraction peaks suggest that the as-prepared samples are well crystallized. And the diffraction peaks from impurities such as cadmium oxide or other cadmium compounds have not been detected, suggesting the high purity of the as-obtained products. A clear difference in the relative intensities of peaks corresponding to various crystallographic planes is visible in the three kinds of CdS films. Compared to the NP XRD pattern (curve b), a sharp increase in the (002) peak intensity than other directions (curve c and d) indicates that the NRs grow preferentially oriented along the [001] direction. It is obvious that the peak intensity of the CdS NP and NR composite film (curve d) is greater than that of the pure CdS NR film (curve c) might due to the compact CdS layer. The EDX spectrum of the CdS composite film is observed in Fig. 3. The S/Cd atomic ratio determined by the relative peaks is 1.15:1, in agreement with the stoichiometric composition of CdS. The observed signal of Si and Sn elements are from the FTO glass substrate.

Fig. 4a shows the TEM image of a single CdS NR. The length of the CdS NR is approximately 500 nm, and the diameter is about 180 nm. The detailed microstructure of this NR is further investigated by HRTEM, as shown in Fig. 4b. The observed 3.55 and 3.36 Å spacing fringes are consistent with the (100) and (002) lattice plane of hexangular wurtzite CdS, respectively. Furthermore, the corresponding SAED pattern which is shown in the top-left inset reveals that the NR is single crystalline in nature. The bottom-right inset of Fig. 4b shows a schematic illustration of the NR structure. The [100] axis is perpendicular to the NR side walls, and the NRs grow along the [001] direction, which are consistent with the XRD pattern.

To better understand the formation process of these CdS NR arrays, the influence of hydrothermal reaction time on the morphology of samples has also been conducted. Fig. 5 shows the FESEM images of CdS NR arrays prepared for the same CBD time (30 min) and different hydrothermal time (8 h, 10 h 12 h and 16 h, respectively). The product obtained at 8 h (Fig. 5a) is the poor hexangular in shape. With the time increasing, more and more hexangularly-faced NRs are obtained. When the reaction time is extended to 14 h, most of the CdS NRs are hexagonal structure as shown in Fig. 1c. And the morphology of products remains the same when the reaction time is 16 h (Fig. 5d).

3.2. The formation mechanism of CdS nanorods

On the basis of understanding the morphology and structure of the as-prepared CdS films, a strategy to achieve the densely and uniformly CdS NR array has been demonstrated through the simple CBD and hydrothermal method. A schematic illustration of the reaction pathways and formation mechanism of different CdS films are listed in Fig. 6. In fact, the formation of CdS films can