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Influence of anionic concentration and deposition temperature on formation of wurtzite CdS thin films by in situ chemical reaction method

Juan Chu [a], Zhengguo Jin [a,*], Weidong Wang [a], Hui Liu [a], Dalong Wang [a], Jingxia Yang [b], Zhanglian Hong [b]

[a] School of Materials Science and Engineering, Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, Tianjin 300072, PR China
[b] State Key Laboratory of Silicon Materials, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, PR China

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ABSTRACT

Nanocrystalline CdS thin films were deposited on glass substrates by a new in situ chemical reaction synthesis using cadmium precursor solid films as reaction source and sodium sulfide based solutions as anionic reaction medium. The influence of the S:Cd molar concentrations in separate cationic and anionic precursor solutions and the deposition temperature on the crystallized structure, morphologies, chemical component and optical properties of the deposited CdS films was investigated by X-ray diffraction, field emission scanning electron microscope, energy dispersive X-ray analysis and UV–Vis spectra measurements. The results show that CdS thin films deposited by the in situ chemical reaction synthesis have wurtzite structure with (0 0 2) plane preferential orientation and this tendency gradually enhances with increase of S:Cd molar concentration ratio. The deposition rate was 80–100 nm thickness per cycle in the range of deposition temperature from 20 °C to 60 °C.

1. Introduction

In the last two decades, a large amount of work has been devoted to study of CdS thin films for their capacity to increase the conversion coefficient of solar cell devices [1–5] and potential in wide applications relating to the ability to adjust electronic band gap energy through particle size [6]. CdS is an n-type semiconductor which has direct band gap (E_g = 2.42 eV) and optical absorption suitable for photovoltaic applications as window coatings in many types of solar cells with absorber materials such as Cu(In, Ga)Se_2 [7], CdTe [8,9] or $CuInSe_2$ [10,11]. Furthermore, CdS nanocrystals are applied for lasers [12], biological labels [13,14], photoconducting cells in sensors [15] and photoelectrocatalysis devices [16–19].

Numerous methods have been developed to prepare CdS nanocrystalline films, typically physical vapor deposition [20–22], magnetic sputtering [23], close spaced sublimation [24], molecular beam epitaxy [25], chemical vapor deposition [26], chemical bath deposition (CBD) [27,28], electrodeposition [29], successive ionic layer adsorption and reaction (SILAR) method [30–32], photochemical deposition [33], screen printing [34], electrostatic assisted aerosol jet deposition [35] and ion layer gas reaction (ILGAR) method [36]. Recent years, there have been increasing efforts in developing new synthesis techniques which particularly have some advantages on green materials, low cost and easy fabrication on a large scale. CBD is a time-efficient method and can deposit high quality CdS thin films on large area substrates. However, the homogeneous nucleation in the reaction solution, which simultaneously was accompanied with the effective heterogeneous nucleation deposition on substrate for thin film formation, took place in the deposition solution, leading to a high proportion of Cd and S precursor source loss and further environmental pollution [26,27]. SILAR is a simple, low cost and less precursor source loss preparation but it is of low time-efficiency and only has about 2–3 nm deposited layer thickness per SILAR cycle [29,30]. So, we suggested whether a new deposition method could be developed, which used SILAR deposition cycles with improved time-efficiency by displacing the thin ion-absorbed layer with a pre-formed and thick cationic precursor solid film. In this work, we described the new synthesis method, named in situ chemical reaction synthesis, to prepare CdS thin films. The method used pre-formed cadmium nitrate solid thin films as cationic reaction source and sodium sulfide based solutions as anionic reaction medium. The effects of anionic concentration, in situ deposition temperature and annealing treatment on crystallization, morphology, stoichiometry and optical properties of the CdS thin films by the in situ chemical reaction synthesis were mainly investigated by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy dispersive X-ray analyzer (EDAX) and UV–Vis spectra measurement.

* Corresponding author. Fax: +86 22 27404724.
E-mail address: zhgjin@tju.edu.cn (Z. Jin).

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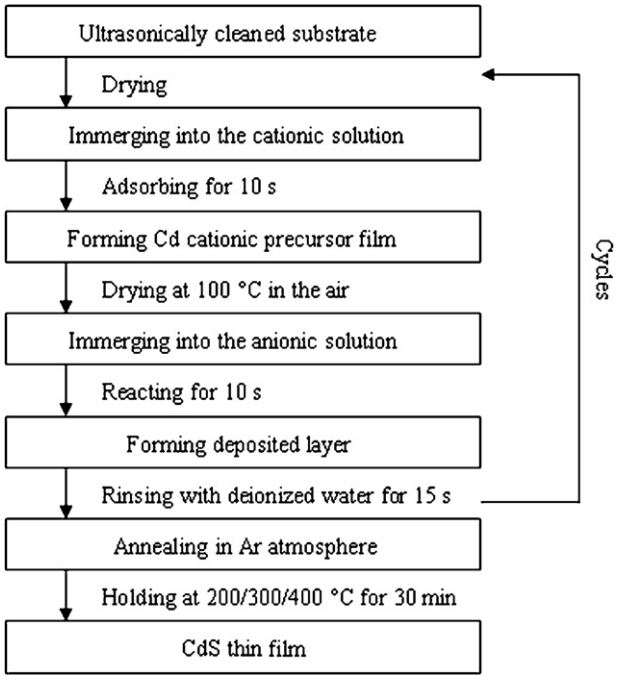

Fig. 1. Flow chart of CdS thin film by in situ chemical reaction process.

2. Experimental

2.1. Chemicals

For in situ deposition of CdS thin films, the following chemicals were used: cadmium nitrate ($Cd(NO_3)_2{\cdot}4H_2O$), sodium sulfide (Na_2S), ethylene glycol monomethylether ($HO(CH_2)_2OCH_3$), butyl alcohol ($CH_3(CH_2)_3OH$), ethanolamine ($HO(CH_2)_2NH_2$) and deionized water. All chemicals are AR grade and directly used.

2.2. Preparation of CdS thin films

Cationic solution for the pre-formed Cd precursor films: 0.15 M $Cd(NO_3)_2{\cdot}4H_2O$ was dissolved into a mixed solution of 15 mL ethylene glycol monomethylether, 3 mL ethanolamine and 2 mL butyl alcohol. Anionic reaction solutions: certain content of Na_2S was dissolved into a mixed solution of 12 mL deionized water and 8 mL ethylene glycol monomethylether, and the Na_2S concentrations were 0.15, 0.30, 0.45 and 0.60 M, respectively. The CdS films were respectively deposited in the four different anionic reaction solutions at solution temperature of 20 °C. To investigate effect of in situ deposition temperature, deposition temperature was altered at 20 °C, 40 °C and 60 °C, respectively, with the fixed Na_2S concentration of 0.30 M. Microscope glass slides of 25 mm × 15 mm × 1 mm were used as substrates, which were ultrasonically cleaned with 30% nitric acid, alcohol and deionized water for 20 min, respectively. The flow chart of preparation of CdS thin films by the in situ chemical reaction process is shown in Fig. 1. At first, Cd^{2+} precursor solid thin films were coated on cleaned glass substrates by dip-drawing method and following drying at oven of 100 °C in the air. Then the coated substrates were immersed into anionic reaction solution for 10 s, where Cd^{2+} reacted with S^{2-} to generate CdS deposited layer. The substrate was washed with deionized water for 15 s to remove counter ions and organic impurity. Above operation cycle was repeated for 2–10 times to investigate film growth. The as-deposited films were annealed at temperatures of 200 °C, 300 °C and 400 °C for 30 min in argon atmosphere, respectively. The processing conditions used in the experiment are listed in Table 1. The chemical reaction formulae involved in the in situ reaction process are given as follows:

$$Cd(NO_3)_2 \rightarrow Cd^{2+} + 2NO_3^- \quad (1)$$

$$Cd^{2+} + n\,HO(CH_2)_2NH_2 \rightarrow Cd[O(CH2)_2NH_2]_n^{2-n} \quad (2)$$

$$Na_2S \rightarrow 2Na^+ + S^{2-} \quad (3)$$

$$Cd[O(CH2)_2NH_2]_n^{2-n} + S^{2-} \rightarrow CdS + n\,HO(CH_2)_2NH_2 \quad (4)$$

2.3. Characterization

X-ray diffraction analysis was carried out using a Rigaku D/Max 2500V/PC X-ray powder diffractometer with CuKα radiation (λ = 1.54178 Å) at a scanning rate of 8°/min ranging from 2θ = 10° to 80°. The surface morphologies and cross section of CdS thin films were observed by Hatchi S-4800 model field emission scanning electron microscope, and the accelerating voltage is 10 kV. The chemical composition of CdS thin film was determined by energy dispersive X-ray analysis (EDAX) using a Genesis XM2 energy dispersive X-ray analyzer attached FESEM. The optical absorption spectra were recorded using TU-1901 UV–Vis spectrophotometer ranging from 200 to 900 nm.

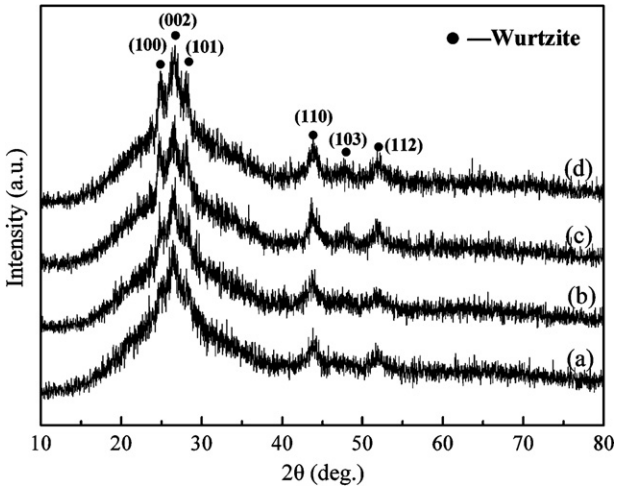

Fig. 2. XRD patterns of CdS thin films deposited with Na_2S concentrations of (a) 0.15 M, (b) 0.30 M, (c) 0.45 M and (d) 0.60 M at 20 °C, 10 dip-cycles and annealed at 200 °C in Ar.

3. Results and discussion

3.1. Influence of Na_2S concentration

Fig. 2 shows the X-ray diffraction patterns of the nano-crystalline CdS thin films deposited with Na_2S concentrations of (a) 0.15 M, (b) 0.30 M, (c) 0.45 M and (d) 0.60 M, respectively, at 20 °C, 10 dip-cycles and annealed at 200 °C in Ar. It is seen that the diffraction patterns are at early stage crystallization of hexagonal wurtzite structure (JCPDS, 41-1049), and the three major peaks at 2θ of 26.5°, 43.2° and 51.9° can be assigned to (0 0 2), (1 1 0) and (1 1 2) planes of the hexagonal phase. With increasing S:Cd molar concentration to 0.30:0.15, another two peaks at 24.9° and 28.2° appear in Fig. 2(b), which can be assigned to plane (1 0 0) and (1 0 1) reflection of hexagonal wurtzite phase. The two characteristic peaks become more definite for the film sample with S:Cd molar concentration of 0.45:0.15 meanwhile the peak at 2θ = 47.8°, corresponding the hexagonal (1 0 3) plane, is also seen in Fig. 2(c). Fig. 2(d) is the XRD pattern of CdS thin film deposited at S:Cd molar concentration of 0.60:0.15, showing that the six main peaks become sharper than the former. So, it can be concluded that the intensities of diffraction peaks increase with rising anionic concentration, which means that the increase of Na_2S concentration has a role on increasing crystallinity of the deposited layer. The Scherrer's relation is used to calculate crystallite size of the CdS thin films:

$$D = \frac{0.94\lambda}{\beta \cos\theta} \quad (5)$$

where λ is the wavelength of incident X-ray, θ is the diffracted angle and β is the full width at the half maximum height. The crystallite size of all the four samples is in the range of 11–12 nm.

Fig. 3 is the X-ray diffraction patterns of the nano-crystalline CdS thin films deposited with Na_2S concentrations of (a) 0.15 M, (b) 0.30 M, (c) 0.45 M and (d) 0.60 M, respectively, at 20 °C, 10 dip-cycles and annealed at 400 °C in Ar. It is seen that the hexagonal wurtzite diffraction peaks of all the films annealed at 400 °C become sharper when compared with those of the samples annealed at 200 °C. Particularly, the intensities of three main peaks of (1 0 0), (0 0 2) and (1 0 1) planes in the XRD patterns are not in agreement