



Chemically deposited ammonia-free cadmium hydroxide thin films



J. Hernández-Borja^{a,*}, R. Ramírez-Bon^b, Y.V. Vorobiev^b, M.A. Hernández-Landaverde^b

^a Universidad de Aeronáutica en Querétaro, Sub-dirección de Ingeniería, Colon 76270, Qro, Mexico

^b Centro de Investigación y de Estudios Avanzados del I.P.N. Unidad Querétaro, Apdo. Postal 1-798, 76001 Querétaro, Qro, Mexico

ARTICLE INFO

Article history:

Received 11 January 2016

Received in revised form 13 June 2016

Accepted 8 July 2016

Available online 10 July 2016

Keywords:

Cadmium hydroxide

Thin films

Chemical deposition

Ammonia free

ABSTRACT

Polycrystalline thin films of cadmium hydroxide $\text{Cd}(\text{OH})_2$ with high purity and good adhesion to the substrate were synthesized by an ammonia free chemical bath deposition method. The as-deposited films have a monoclinic crystalline structure with lattice constants $a = 6.5768 \text{ \AA}$, $b = 10.2704 \text{ \AA}$, $c = 3.4125 \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 120.16^\circ$, $\gamma = 90.00^\circ$, and crystallite size $26.1 \pm 0.9 \text{ nm}$. The cubic phase of cadmium oxide with lattice constants $a = 4.7155 \text{ \AA}$ and crystallite size of $10.9 \pm 0.9 \text{ nm}$ was obtained by heating the as-deposited films at 220°C . The absorption bands in the $3500\text{--}3600 \text{ cm}^{-1}$ range observed in the infrared spectra of the as-deposited films were used to detect the presence $\text{Cd}(\text{OH})_2$ compound. The possible ways to optimize the synthesis of $\text{Cd}(\text{OH})_2$ to be used as precursor for production of chalcogenide films is discussed.

© 2016 Published by Elsevier B.V.

1. Introduction

Cadmium hydroxide $\text{Cd}(\text{OH})_2$ is a compound semiconductor with wide energy band gap of 3.2 eV and high electrical conductivity, which has been studied for applications in solar cells, sensors, transparent electrodes, batteries, etc. [1–6]. It can also be used as a precursor material to obtain cadmium oxide and some chalcogenides semiconductors such as CdS, CdO and CdSe, providing the appropriate substitution reactions [7–12]. Based on this, in previous work we have designed a technique for producing thin films of CdTe for photovoltaic applications by chemical bath technique from precursor thin films of CdO– $\text{Cd}(\text{OH})_2$ [13]. This, in order to produce absorbent layers of CdTe at low temperatures and without high vacuum equipment; however, utilization of unstable reagents such as hydrogen peroxide produces impurities in the precursor films that are limiting the implementation of absorbent layers. A similar procedure was reported to obtain CdSe films from CdO– $\text{Cd}(\text{OH})_2$ films [14]. In this paper we established formulations to optimize the synthesis of thin films of $\text{Cd}(\text{OH})_2$ to improve the purity, adhesion and reproducibility thereof.

Thin films of CdO/ $\text{Cd}(\text{OH})_2$ with hexagonal structure of $\text{Cd}(\text{OH})_2$ were deposited with the SILAR method by Aytunç Ateş [15] using cadmium-aqueous ammonia complex ions ($[\text{Cd}(\text{NH}_3)_3]^{2+}$), where they observed decrease in energy gap from 3.59 to 2.13 eV and changes of resistivity from 10^5 to $0.2 \text{ } \Omega\text{-cm}$ when performing heat treatment to get the cubic phase of cadmium oxide. R.S. Mane [16] synthesized nanocrystalline thin films of $\text{Cd}(\text{OH})_2$ with monoclinic crystalline structure using chemical processes at low temperatures with extra pure cadmium chloride and ammonia chemicals, and triply distilled water as solvent.

Xinsheng Peng [17] deposited ultrathin nanofibrous films of thickness $<60 \text{ nm}$ from the dispersion of cadmium hydroxide nanostrands with a diameter of 1.9 nm and the length of a few micrometers.

Our experiments are essentially different from those described in the literature in the sense that we optimize the synthesis of $\text{Cd}(\text{OH})_2$ thin films, as precursors used for the synthesis of chalcogenide semiconductors by chemical bath deposition technique. The advantages of this method allow the reduction of production costs and energy consumption, to give the possibility to deposit films in large area substrates, without increasing considerably the cost. We have also reduced environmental impacts by using ammonia-free formulation [18,19], because ammonia is highly volatile, toxic and dangerous to the environment. Furthermore, the volatility of ammonia changes the pH of the solution along the deposition process thus producing thin films with irreproducible properties.

2. Experimental procedure

For the synthesis of $\text{Cd}(\text{OH})_2$ thin films we used Corning glass substrates with a tin oxide layer located on one side of the substrate; we identified this layer by means of fluorescence, by impinging light from an ultraviolet lamp at an angle incidence of 45° on the substrate. In previous studies, we have observed better adhesion and homogeneity over this layer of chemically deposited chalcogenide semiconductors thin films [18]. The substrates were washed with soap and rinsed in distilled water several times, then were cleaned in ultrasonic bath for 15 min and dried in nitrogen atmosphere.

Two different recipes were used to deposited thin films of cadmium hydroxide, which we called Ha and Hd. The growth solution for Ha films contained 30 ml of cadmium chloride CdCl_2 (0.1 M), 20 ml of sodium citrate $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (0.6 M) and 12 ml of potassium hydroxide

* Corresponding author.

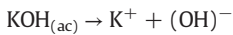
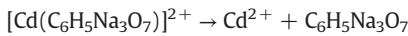
KOH (0.51 M). For the case of Hd films we used 7.5 ml of CdCl₂ (2 M), 46 ml of Na₃C₆H₅O₇ (1.3 M) and 9 ml of KOH (2 M). In each series, chemical bath temperature was 70 °C, adjusting the deposition time to 3 h, determined by the depletion of the growth solution and adhesion of thin films to the substrate. In both cases, the Cd(OH)₂ films were homogeneous with whitish color and good adhesion to the substrate.

The semiconductor films obtained were characterized by X-ray diffraction using the equipment RIGAKU Ultima IV, Cu-K_{α1}/K_{α2} radiation (λ = 1.54059 / 1.54442 Å) with 40 kV and 30 mA, and software Winjade by MDI. In situ XRD patterns of the films were measured in the 25–390 °C temperature range. Optical transmission spectra were recorded in the frequency range 250–4000 cm⁻¹ using a Perkin Elmer FTIR Spectrum GX. Surface morphology was extent using Scanning Electron Microscope SEM (JEOL JSM-5800LV). Differential Scanning Calorimeter DSC 822e MT was used between 30 and 600 °C.

3. Results and discussion

3.1. Chemical reactions

The proposed reaction mechanism for the synthesis of cadmium hydroxide is as follows:



$\text{Cd}^{2+} + 2(\text{OH})^- \rightarrow \text{Cd}(\text{OH})_2$
 where Cd(OH)₂ of the last reaction can precipitate in bulk to form solution colloid or on the surface of the substrate. Whereby, there are two different mechanisms for thin film growth, sedimentation of colloids also called cluster by cluster and direct reaction of species in the substrate surface, also called ion by ion process. However, in the synthesis of thin films by chemical bath technique it is common the occurrence of both mechanisms during the film growth process [20].

3.2. Structural investigation

Fig. 1 shows the X-ray diffraction pattern of the thin films of the series Ha, where we can see an intense diffraction peak at 20.6° and other weaker diffraction signals at 32°, 35.5° and 36.6°, which are consistent with the 2θ values found in the literature for the diffraction peaks of the monoclinic phase of cadmium hydroxide (JCPDS #40-0760). The crystallite size was calculated using the software Winjade by MDI resulting in 27.6 nm. In order to determine the transition temperature to the cadmium oxide phase, in situ X-ray diffraction measurements were performed on this cadmium hydroxide film in the 30–390 °C temperature range, and the results are shown in Fig. 2. At the bottom, the diffraction patterns of cadmium hydroxide (JCPDS #40-0760) and cadmium oxide (Monteponite, JCPDS #5-0640) powders were plotted. As can be seen, the XRD patterns measured at 30 and 130 °C display the diffraction peaks of the cadmium hydroxide phase; meanwhile the patterns measured at 220, 225, 290 and 390 °C display the diffraction peaks of the monteponite crystalline phase of cadmium oxide. This is a cubic crystalline phase with diffraction peaks at about 33, 38, 55, 66 and 69°, as observed in these patterns, which are related with the

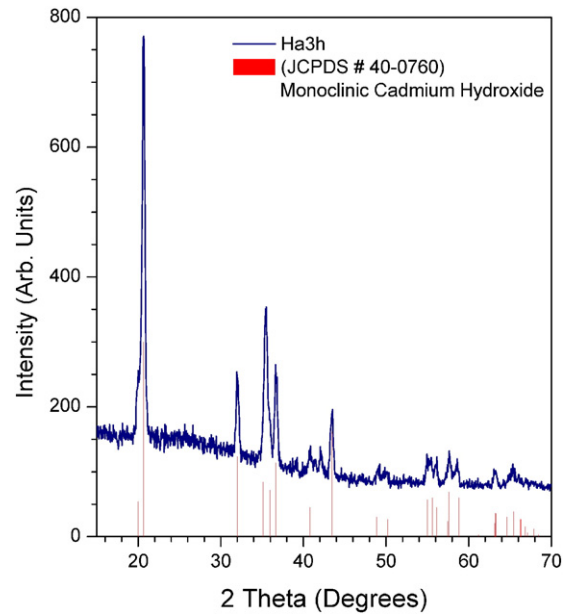


Fig. 1. Pattern X-ray diffraction of thin films of Cd (OH)₂ of the Ha series.

(111), (200), (220), (311) and (222) crystalline planes, respectively. Therefore, there is a phase transition between 130 and 220 °C, produced by the thermal oxidation of cadmium hydroxide phase. At higher temperature, the diffraction peaks of cadmium oxide get narrow, with higher intensity, evidencing the enhancement of the crystallinity of this phase. All the XRD patterns were analyzed with Winjade software to determine some crystalline parameters of both phases and the evolution with temperature. The results are shown in Table 1, where it is observed that the crystallite size and the unit cell volume of the monoclinic phase of Cd(OH)₂ does not change significantly in thin films at temperatures < 130 °C. For the cubic phase of CdO, the crystallite size increases from 10.9 to 15.7 nm as the measurement temperature increases from 225 °C to 390 °C. For both phases, the lattice constants, and then the unit cell volumes, are larger than those for bulk showing some expansion of the films crystalline lattice, probably due to residual stress.

The crystalline phase transition with temperature was also analyzed by DSC measurements performed on the precipitated Cd(OH)₂ powder

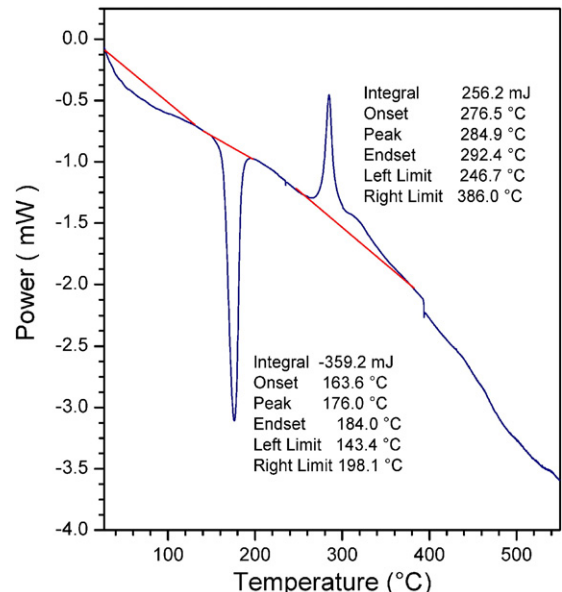


Fig. 2. DSC precipitates Cd (OH)₂ of the Ha series.

Download English Version:

<https://daneshyari.com/en/article/1663833>

Download Persian Version:

<https://daneshyari.com/article/1663833>

[Daneshyari.com](https://daneshyari.com)