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ASIAN JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN: 0976-3376

Asian Journal of Science and Technology
Vol. 07, Issue, 11, pp.3820-3823, November, 2016

RESEARCH ARTICLE

MORPHOLOGICAL EVOLUTION OF NANOCRYSTALLINE CdS THIN FILMS SYNTHESIZED BY TWO DIFFERENT CHEMICAL DEPOSITION TECHNIQUES

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ARTICLE INFO

Article History:
Received 17th August, 2016
Received in revised form
19th September, 2016
Accepted 02nd October, 2016
Published online 30th November, 2016

Key words:

Cadmium sulfide thin films,
Chemical bath deposition,
SILAR, Morphology.

ABSTRACT

Nanocrystalline thin films of cadmium sulfide (CdS) have been studied extensively in view of their potential industrial applications. Notwithstanding to this, this material is also important both academically as well as scientifically. In this work, we report the synthesis and morphological evolution of nanocrystalline CdS thin films prepared by chemical bath deposition (CBD) and successive ionic layer adsorption and reaction (SILAR) method. The films were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and optical absorption measurements. X-ray diffraction patterns confirm the nanocrystalline nature of the deposited films with hexagonal structure. The average crystallite size of the films prepared by CBD and SILAR technique is found to be 22.50 nm and 33.70 nm, respectively. FE-SEM studies revealed the significant change in the surface morphology of the deposited nanocrystalline CdS thin films with the deposition technique. The optical properties were studied by measuring the absorption spectra. The band gap is 2.36 eV and 2.25 eV for the nanocrystalline CdS thin films prepared by CBD and SILAR technique, respectively.

INTRODUCTION

Cadmium sulfide (CdS) is an interesting II–VI semiconductor material that has been studied for last few decades, possesses n-type electrical conductivity, suitable for applications in various fields such as solar energy conversion and optoelectronic devices (Moualkia *et al.,* 2009). Also it has been regarded as material with many attractive properties, such as direct bandgap of the order of 2.4 eV and moderate resistivity (Khomane, 2010). Consequently, this compound offers an important number of applications such as solar cells (Repins *et al.,* 2008), optoelectronic devices (Wu *et al.,* 2007), photodetector (Deng *et al.,* 2014; Duncan *et al.,* 1974) and thin film transistors (Dondapati *et al.,* 2014), etc. Different methods have been employed in the fabrication of high quality CdS thin films such as thermal evaporation (Singh *et al.,* 2016), aerosol assisted chemical vapor deposition (AACVD) (Mlowe *et al.,* 2015), pulsed laser deposition (Liu *et al.,* 2016), ion-beam sputtering (Liang *et al.,* 2013), electrochemical deposition (Maricheva *et al.,* 2016), sol-gel spin coating method (Munirah *et al.,* 2013), spray pyrolysis (Yuksel *et al.,* 2013), electron beam evaporation technique (Sivaramamoorthy *et al.,* 2010), etc. However most of these methods required expensive sophisticated instrumentations and vacuum environment for the deposition of thin films. So now a day's low cost deposition methods have been extensively used for the preparation of good quality metal chalcogenide and oxide thin films. Among various chemical methods, CBD and SILAR recently emerged as the method for the deposition of metal chalcogenide thin films (Pawar *et al.,* 2011; Pathan *et al.,* 2004). These methods are presently attracting considerable attention because simple equipments like hot plate with magnetic stirrer are needed. The starting chemicals are commonly available and cheap and large area deposition becomes possible. Most of researchers utilized either of these methods for the preparation of CdS thin films (Kumarage *et al.,* 2016; Abdullah *et al.,* 2012; Mukherjee *et al.,* 2015; Chaudhari *et al.,* 2015). In the present investigation, we attempt to synthesize the nanocrystalline CdS thin films by using both the chemical processes namely, CBD and SILAR techniques, for the study of morphological evolution of nanocrystalline CdS thin films.

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MATERIALS AND METHODS

Nanocrystalline CdS thin films preparation

In the present work, nanocrystalline CdS thin films were grown on commercially available, optically pure glass plates

(25mm x 75mm x 1.35mm) by CBD and SILAR techniques. Before the deposition of CdS thin films on glass substrates, a cleaning process was applied to the substrates. Initially the glass substrates were put into a beaker containing distilled water and kept there for 10 min to remove contaminants such as dust on their surfaces. Then the substrates were degreased by chromic acid and rinsed with deionised water. Finally substrates were ultrasonically cleaned with deionised water before deposition of thin film. The deposition of nanocrystalline CdS films by using the CBD technique in a cadmium sulfate–ammonia-thiourea system consist of: complexation of cadmium cations by ammonia and the consecutive reaction with the sulfide ions provided by hydrolysis of thiourea. The chemical bath contains aqueous solution of 10ml of 0.5M cadmium sulfate complexed with ammonia and 10ml of 0.5M thiourea. The pH of the mixture was maintained at nearly 11 to 12. Then, mixture is stirred well. This reaction mixture was transferred into another beaker, in which the precleaned substrates were kept vertically. The deposition was carried out in a 50 ml beaker at 80^{o}C temperature for a deposition time of 50 minute. Thereafter substrate coated with CdS was removed, rinsed with deionised water, and dried in open air at room temperature for 10 minute. Film obtained was uniform, well adherent and yellowish in color. The thickness of the optimized thin films was ≈ 265 nm.

Cadmium chloride monohydrate ($CdCl_2.H_2O$), sodium sulfide (Na_2S) and ammonium hydroxide (NH_4OH) were used for the deposition of CdS thin films by using SILAR. For the deposition of CdS thin film, 0.2M $CdCl_2$ solution (pH~5.9) is used as cationic precursor complexed with 1M NH_4OH and 0.1M Na_2S solution (pH~11.5) as anionic precursor. For preparation of CdS film, a well-cleaned glass substrate was immersed in the cationic precursor solution ($CdCl_2$) for 30 seconds, causing cadmium ions to be adsorbed on the surface of the glass substrate. This substrate was then immersed in deionised water for 10 seconds. This is done to remove the loosely bounded Cd^{2+} ions from glass substrate. The substrate was then immersed in the anionic precursor solution (Na_2S) for 30 seconds. Sulfide ions reacted with the adsorbed cadmium ions on the glass substrate. The substrate was then immersed in deionised water for 10 seconds. Thus, one cycle of CdS film deposition is completed. Deposition was carried out at room temperature. For this particular study we have deposited CdS thin films with 60 SILAR cycles. After 60 SILAR cycles an adherent and uniform CdS thin film of thickness ≈360 nm is obtained on the glass substrate.

Characterization

The CdS thin films prepared by using CBD and SILAR techniques were further characterized by using XRD, FE-SEM and UV-VIS spectroscopy. X-ray diffraction (XRD) analysis is carried out for the determination of structure and crystallite size using Bruker AXS, Germany (D8 Advanced). The surface morphology and chemical composition of the films were analyzed by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS) using S-4800 type-II (Hitachi High Technology Corporation Tokyo, Japan). The optical properties of the films were determined by JASCO V-630 UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

Structural studies

The grain size and crystal structure of the CdS nanocrystalline thin films were determined using X-ray diffraction measurements. CdS is known to exist in either cubic or hexagonal structure or sometimes a mixture of both phases (Abdullah *et al.,* 2012; Shende *et al.,* 2015; Prabahar *et al.,* 2005; Liu *et al.,* 2010). Fig. 1(a) and (b) shows a typical XRD pattern of nanocrystalline CdS thin films prepared, by CBD and SILAR technique respectively, on glass substrate at optimized preparative parameters. The data are further analyzed and it is found that CdS films deposited by CBD and SILAR technique are polycrystalline in nature with hexagonal crystal structure. For CBD grown CdS thin films, two major peaks at 2θ ≈ 21.77^{o} and 25.31^{o}, assigned, respectively, to the (1 0 3) and (2 0 2) planes of hexagonal phase (JCPDS 02-0549). Also from XRD pattern of CdS thin films grown by SILAR, two major peaks observed at 2θ ≈ 37.58^{o} and 43.82^{o} corresponds to hexagonal phase for the (1 0 2) and (1 1 0) planes respectively (JCPDS 01-0783). Significant change in the peak position and peak intensity was found in the XRD pattern of CdS thin films grown by SILAR technique as compared to the CdS film grown by CBD. For the intense peaks observed in XRD pattern, we calculated the crystallite size using Scherrer's formula (Moualkia *et al.,* 2009) as given below,

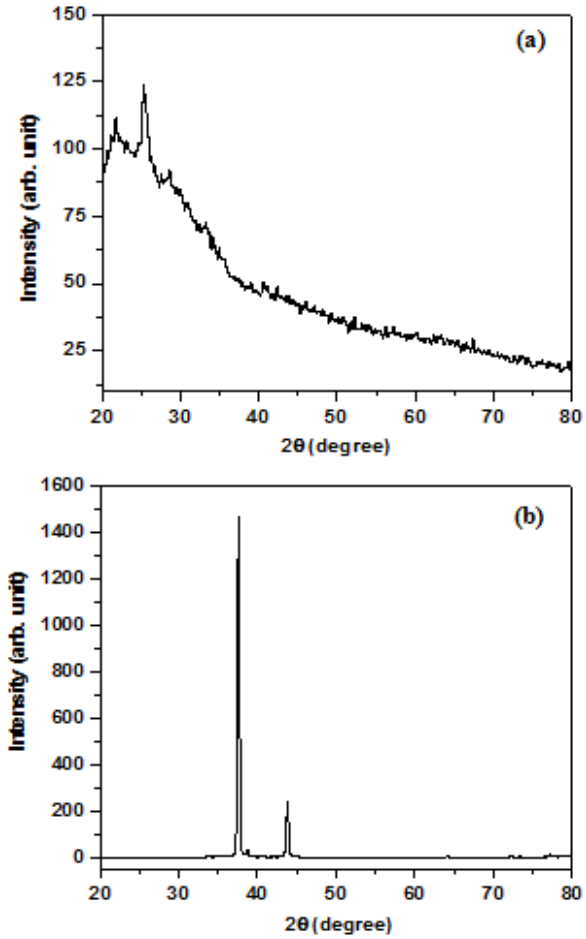

Fig. 1. XRD Patterns of nanocrystalline CdS thin films prepared by using (a) CBD and (b) SILAR technique

Where, λ is wavelength of X-ray; β is broadening of diffraction line measured at full width at half of the peak maxima in radians. K is a constant (0.94) and θ is Bragg's angle. The calculated average crystallite size is 22.50 nm for the film deposited by CBD technique and 33.70 nm for the film deposited by SILAR technique at optimized preparative parameters.

Surface morphology

Surface morphology of the nanocrystalline CdS thin films deposited by CBD and SILAR studied with the FE-SEM images shown in the Figures 2(a) and (b) respectively. This study shows a clear dependence of film morphology on the deposition technique. From Fig. 2(a), flake like morphology was found for the CdS film deposited by using CBD technique. Such kind of morphology is very useful for photoelectrode degradation and photoelectrochemical based solar cells (Shende *et al.,* 2015; Patil *et al.,* 2010). On the other hand significant change in the surface morphology was found in case of CdS film grown by SILAR technique shown in Fig. 2(b). Also it has been found that, the surface of the prepared films is fairly smooth, without cracks and pinhole free with spherical grains and with dense surface morphology covering entire substrate surface area and strong adherence to the substrates.

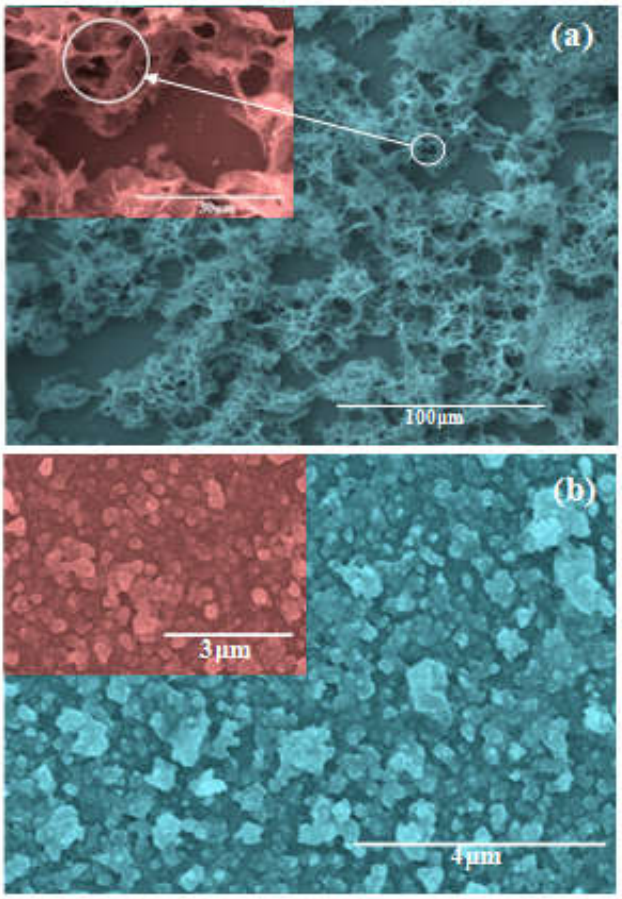

Fig. 2. FE-SEM images of nanocrystalline CdS thin films prepared by using (a) CBD and (b) SILAR technique

Optical studies

Fig.3 shows a plot of absorption coefficient versus wavelength for nanocrystalline CdS thin films, prepared by using CBD and SILAR techniques. The spectrum shows absorption edge at around 550 nm and 630 nm wavelength for CBD and SILAR grown nanocrystalline CdS thin films respectively. The edge is seen to be strongly red shifted.

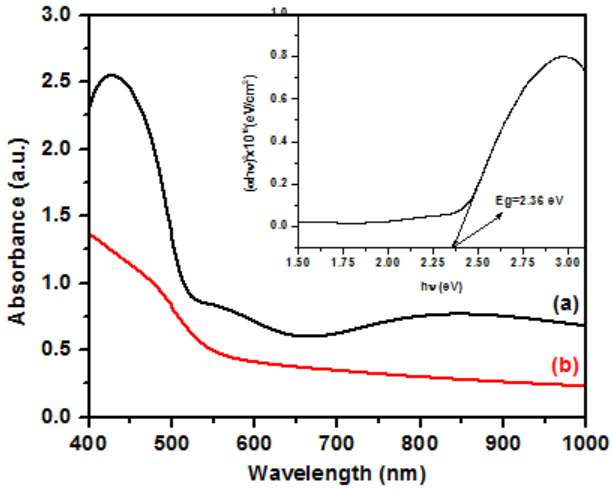

Fig. 3. Room temperature optical absorption spectra of nanocrystalline CdS thin films prepared by using CBD and SILAR technique

The theory of optical absorption gives the relation between the absorption coefficient α and the photon energy hν, for direct allowed transition as (Mehta *et al.,* 2009), where hν is the photon energy, E_g is the optical bandgap, A is a constant. Plot of $(\alpha h\nu)^2$ versus hν shown in inset of Fig. 3 for a CBD grown CdS thin film, which is linear at the absorption edge, confirming the direct band gap material. The direct bandgap of CdS thin films deposited with CBD and SILAR techniques are determined by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$. The energy band gap is of the order of 2.36 eV and 2.25 eV for CBD and SILAR grown nanocrystalline CdS thin films, which closely agrees with the standard value reported for CdS thin films deposited by CBD (Tec-Yam *et al.,* 2011; Sharkey *et al.,* 2011) and SILAR (Chaudhari *et al.,* 2015). The greater band gap of CdS film deposited by CBD technique is might be due to the smaller crystallite size as compared to that deposited by SILAR technique.

Conclusion

Inexpensive deposition techniques namely CBD and SILAR successfully utilized for the deposition of nanocrystalline CdS thin films. XRD and FE-SEM studies revealed the significant change in the diffraction pattern and morphology of the deposited nanocrystalline CdS thin films with the deposition technique. Optical study reveals variation in the band gap from 2.36 eV to 2.25 eV for the nanocrystalline CdS thin films prepared by CBD and SILAR technique, respectively.

Acknowledgement

The authors sincerely acknowledge University Institute of Chemical Technology (UICT), North Maharashtra University, Jalgaon for providing the characterization facilities. The author NMG sincerely acknowledges Principal Dr. R. P. Borkar, Government College of Engineering, Jalgaon for his constant encouragement and kind support in the research activity. The authors would also like to thank Principal, C.H.C. Arts, S.G.P. Commerce and B.B.J.P. Science College, Taloda for providing the characterization facilities.

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