Research Article

Synthesis and Study of CdS Thin Films Prepared with Different KMnO_4 Activation Time

Sarveswaran Thangarajan,¹ Gopinathan Chellachamy,² Saravanakumar Kulendran,³ Pandi Pitchai,² and Mahalakshmi Kandasamy⁴

¹PG and Research Department of Physics, The Madura College, Madurai, Tamil Nadu 625011, India

²Department of Solar Energy, Madurai Kamaraj University, Madurai, Tamil Nadu 625021, India

³Department of Physics, Kongunadu Arts and Science College, Coimbatore, Tamil Nadu 641029, India

⁴Department of Physics, Providence College for Women, Coonoor, Tamil Nadu 643104, India

Correspondence should be addressed to Sarveswaran Thangarajan; tsarveswaran@gmail.com

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The growth and properties of cadmium sulfide (CdS) thin films were prepared in a controlled manner using chemical bath deposition (CBD) method for different KMnO_4 activation time such as 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min on glass substrates. CdS thin films are deposited on KMnO_4 activated glass substrates at 85°C with pH value of 10 for 30 min deposition time. In the chemical bath deposition (CBD) technique, KMnO_4 activation time plays an important role in the growth of the CdS film. The structure of the CdS film changes with respect to the rate of deposition. The size of the particles is affected by the nucleation rate if the solution does not contain the constant number of Cd^{2+} and S^{2-} ions throughout the deposition process. This change in structure of CdS is confirmed by the XRD, SEM, and AFM analysis, and the ion-by-ion nucleation growth is also examined. The optical property of the prepared CdS thin film is scrutinized using UV-Vis-NIR absorption analysis.

1. Introduction

In recent research, synthesis of 3D complex structures and studies on their properties are significant and need to be developed, because the structures with complexity exhibit more novel properties, which would be useful for the existing as well as novel device applications. Kokotov and colleague [1, 2] synthesized a 3D flower-like structured CdS/ZnO composite film by one-step chemical bath deposition after forming KMnO_4 seed layer.

The glass substrate can be subjected to different surface activation techniques. One of the common techniques is the use of seeding layers to facilitate nucleation. Although the nature of the substrate surface is expected to be more essential for heteronucleation, the film formation from chemical baths operating in the homogenous nucleation regime can also be influenced by the glass substrate surface properties such as

hydrophilicity, pH, and roughness due to differences in the tendency of colloids from solution to adhere to the surface.

Potassium permanganate (KMnO_4) slowly decomposes in water producing MnO_2 and O_2 . This decomposition is strongly accelerated by the acid, base, or the presence of the oxide itself. Alcohols can also reduce permanganate. The colloidal $\text{Mn}(\text{O})\text{OH}$ adsorbed on the glass substrate promotes CdS film growth, while the greater part of the colloid in the solution results in homogeneous CdS nucleation. The seed layers also promote columnar growth [2, 3].

A variety of chemical bath depositions are used for deposition on different polymer surfaces subjected to various activation treatments. The most effective treatment is immersing the substrate in KMnO_4 for different time. KMnO_4 activated glass surfaces that have been treated in this manner then react easily with other reagents, and a properly coated glass surface is obtained.

We hardly find any report on the synthesis of CdS thin films that are prepared using CBD method for different KMnO_4 activation time such as 5, 10, 15, 20, 25, and 30 min on glass substrates. In this study, CdS thin films were synthesized by a simple CBD method.

2. Experimental Works

2.1. Substrate Activation. In this study CdS films were deposited on soda-lime glass slides. The cleaning of the substrate was done by the sequential steps of dipping the slides in chromic acid for 20 min, cleaning with soap solution for 5 min, and then immersing in deionized water in an ultrasonic bath for 15 min. Before deposition, the substrate was activated with a seed layer of Mn-(hydroxy) oxide. For the formation of Mn(O)OH seed layer, we adopted the procedure reported by Kokotov and Hodes [2]. For the activation of substrate, a beaker containing 50 mM of KMnO_4 solution was taken, and 50 μL of n-butanol was added per 20 mL of KMnO_4 solution and was kept in a water bath at 85°C for 5, 10, 15, 20, 25, and 30 min to activate the glass substrates. After activation, the substrates were taken out and kept in an ultrasonic bath for 15 minutes. The activated wet glass slides were then dried and used for coating. The permanganate treated substrates at 85°C were used for the deposition of CdS films.

2.2. Preparation of Thin Films. It was observed from the previous results that the decrease in the concentration of precursors resulted in the decrease of particle size on the nonactivated glass substrate. This was due to the slow kinetic transport during heterogeneous nucleation growth, which initiated an ion-by-ion mechanism of growth instead of the cluster-by-cluster mechanism [4]. Hence, in addition to the seed layer formation and to have ion-by-ion growth mechanism, the concentration of the solution was reduced.

The chemical bath contained an aqueous solution of 0.4 M of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$) and 0.5 M thiourea ($\text{CH}_4\text{N}_2\text{S}$) taken as the precursor for CdS film formation. Ammonium hydroxide (14.8 N) was added as a reducing agent to liberate sulphur ion from thiourea and to maintain the pH of the solution. The pH of the solution was maintained at 10. The deposition lasted for 30 min at a temperature of 85°C . The films were deposited on the permanganate treated substrates.

During the deposition, colour of the solution gradually changed from transparent to dark yellow within 40 to 45 minutes. Once the colour change occurred, ammonia was added drop by drop using a burette and the activated substrate was inserted at the same time. The substrate was placed at 90° in the solution for 30 min. This procedure was repeated for all the activated glass substrates.

3. Result and Discussion

3.1. Structural Studies. XRD pattern of CdS thin films were recorded using Philips X'PERT PRO powder diffractometer with Cu as the target in 2θ range of 10° – 70° in steps of 0.05° as the interval. The intensity of CdS appropriately increased with

FIGURE 1: X-ray diffraction pattern of CdS thin film by CBD with different glass substrate activation time.

respect to substrate KMnO_4 activation time. In Figure 1, the 2θ values confirmed the presence of CdS, and the cubic phase was confirmed by the presence of diffraction peaks (1 1 1) at a 2θ value of 26.77° , 26.79° , 26.72° , 26.79° , 26.70° , and 26.68° in the deposited CdS thin films (as shown in JCPDS number 42-1411). The cubic phase occurred due to the reduction in size of the particle during ion-by-ion deposition mechanism. Throughout the deposition process S/Cd decreased gradually. The grain size of the film was calculated from the line broadening in the XRD pattern by using Scherer's formula [5, 6] and is shown Table 1. The 5 min KMnO_4 substrate activated CdS thin film is amorphous in nature as shown in Figure 1. Moreover, the KMnO_4 substrate activation increases 10 min–30 min; the XRD profile of the CdS thin films shows crystalline nature cubic CdS (zincblende) structure is increased due to the preferred orientation of deposition. Dislocation density and lattice strain were also calculated for the peaks of CdS thin film samples using the formulas $\delta = 1/D^2$ and $\epsilon = \beta \cdot \cos \theta/4$, and the values are given in Table 1.

3.2. Optical Studies (UV Spectral Analysis). CdS deposited on permanganate treated substrates was analysed by optical absorbance and transmission studies in the range of 300–700 nm as shown in Figure 2. Figure 2(a) shows the optical absorption for substrate activation time, and the maximum peak was observed at 15 min. A Tauc plot $(\alpha h\nu)^2$ as function of photon energy ($h\nu$) for CdS thin films with various substrate activation time is shown in Figure 3 [6, 7], and the optical energy gaps are shown in Table 1. There is a change in CdS band gap due to a change in different KMnO_4 activation time conditions [8]. The position of both maxima and minima for reflection and transmission cases can be obtained from Figure 2(b) denoting transmission spectra as a function of wavelength

TABLE 1: The calculated grain size, refractive index, extinction coefficient, and thickness of CdS thin film prepared by CBD.

KMnO ₄ activation time	2θ (°)	FWHM (°)	d -spacing (Å)	$\delta \times 10^{15}$ lines/m ²	ϵ lattice strain $\times 10^{-2}$	D (nm)	E_g (eV)	t (nm)	n	Average size of particle (nm)
5	26.77	0.4	3.272	2.39	9.72	20.42	2.45	391	1.69	102.5
10	26.79	—	3.325	—	—	—	2.53	158	2.45	91.07
15	26.72	0.08	3.334	0.09	1.94	102.11	2.49	263	2.48	91.11
20	26.79	0.21	3.324	0.66	5.10	38.90	2.42	327	2.14	90.77
25	26.70	0.70	3.340	7.34	17.02	11.67	2.30	305	2.34	89.14
30	26.68	0.18	3.337	1.60	4.37	24.95	2.40	200.4	3.00	81.25

FIGURE 2: (a) Optical absorption spectra of CdS thin films for different KMnO₄ activation time. (b) Optical transmission spectra of CdS thin films for different KMnO₄ activation time.

(λ). If, for the transmission cases, m th and $(m + 1)$ th orders of maxima occur at wave lengths λ_1 and λ_2 at normal incidence ($\theta = 0$), then [9, 10]

$$t = \frac{\lambda_1 \lambda_2}{2n_f (\lambda_1 - \lambda_2)}. \quad (1)$$

In this study, thickness of the films was determined from the optical transmission spectrum using (1).

The refractive index (n) was calculated at different wavelengths using the following relation:

$$n = \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})}, \quad (2)$$

where R is the reflectance.

The value of reflectance was calculated by the following relation [11]:

$$A + T + R = 1, \quad (3)$$

where A is the absorbance, T is the transmittance, and R is the reflectance.

3.3. SEM Morphological Analysis. The morphology of the CdS film strongly depends on the conditions such as KMnO₄ concentration, activation time, and addition of reducing agents. The variations in morphology for the CdS deposits on glass substrates activated under different KMnO₄ activation time 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min, respectively, are summarized in Figure 4. The deposited CdS thin films were observed by SEM micrographs (VEGA 3 TE SCAN), as seen in Figure 4, and there is clear evidence that the surface had distinct features composed of sphere-like structures. CdS is distributed well within the range of 80–100 nm. The void space decreased with respect to increase in the activation time, and fine spherical structures were improved. Films with a smooth surface were obtained as the activation time gradually increased. Thus, activation time influenced the preferential growth orientation of the film, which in turn modified the surface morphology of the film. Average size of the particle for the activation time of 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min was 102.5 nm, 91.07 nm, 91.11 nm, 90.77 nm, 89.14 nm, and 81.25 nm, respectively.

FIGURE 3: A plot $(\alpha h\nu)^2$ as function of photon energy ($h\nu$) for CdS thin film for substrate activation time.

3.4. AFM Analysis. The particle size calculated from the AFM images (Figure 5) for the CdS thin films on KMnO_4 activated glass substrate was 101.8 nm. Nonuniform distribution of clusters appeared and porosity was observed in the film. This may cause reduction of density of the film. This nonuniform distribution of clusters created more up and down alignment

of the crystallites, which increased the roughness of the film to around 5.6 nm (Figure 6).

3.5. EDAX Analysis. EDAX analyses were performed for the elemental compositional analysis of the CdS films. The EDAX spectrum observes the characteristic peaks corresponding to

FIGURE 4: SEM micrograph of CdS thin film by CBD for different glass substrate activation time 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min.

FIGURE 5: AFM image of CdS film on KMnO_4 activated substrate at 30 min.

the binding energy of the elements. Figure 7 shows the EDAX spectrum showing strong peaks for Cd and S. The spectrum confirmed that the films were mainly composed of Cd and S. From the observed EDAX analysis, the average atomic percentage of Cd : S was found to be almost stoichiometric in nature with the Cd% of 52 and S% of 48.

4. Conclusion

CdS thin films were prepared using CBD method for different KMnO_4 activation time such as 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min on glass substrates. The cubic phase CdS structure was analysed by the X-ray diffraction study. The

FIGURE 6: Roughness of CdS film on KMnO_4 activated substrate at 30 min.

FIGURE 7: EDAX spectrum of the CdS thin films prepared by CBD for KMnO_4 activation time of (a) 5 min, (b) 10 min, (c) 15 min, (d) 20 min, and (e) 25 min.

uniform size of the particles having spherical shape was observed from the scanning electron microscope. Substrate activation time affected the void space of the thin film, and shape of fine spherical particles was improved. Films with a smooth surface were obtained as the activation time gradually increased. Thus, activation time influenced the preferential growth orientation of the film which in turn modified the surface morphology of the film. The optical absorbance and transmittance were also affected by the KMnO_4 activation time.

Competing Interests

The authors declare that they have no competing interests.

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