

Effects of acids on chalcogenide (cadmium sulfide) thinfilms by chemical bath dip coating techniques

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Among various semiconductor nanoparticles, nano-sized cadmium sulfide (CdS) thin films are the most frequently studied material. Cadmium sulfide thin films are fabricated by chemical bath dip coating method using citric and tartaric acid respectively. The synthesized thin films have been characterized by ultraviolet-visible (UV-Vis), x-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX) spectrum. Results are found that the absorption peak value of CdS thin films were blue shifted and surface smoothness also increases due to the reaction with acids, like citric and tartaric acids.

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Keywords: Cadmium sulfide, Citric acids, Tartaric acids, UV-Vis, XRD, SEM, EDAX, etc

1. Introduction

Semiconductor technology is used in many fields particularly the photovoltaic solar cell field has been identified as one of the most important areas. CdS has direct band gap energy of 2.42 eV at room temperature. Moreover, it has been known as one of the most promising photo-sensitive materials owing to its unique photochemical activities and strong visible-light absorption and emission [1].

In this present work, reaction of cadmium sulfide with acids is made to prepare thin films onto a well cleaned glass substrate by CBD dip coating method. This is characterized with the crystallite size and structures were studied by the XRD pattern and optical properties of the thin films were studied by the UV-Vis values.

2. Experimental studies

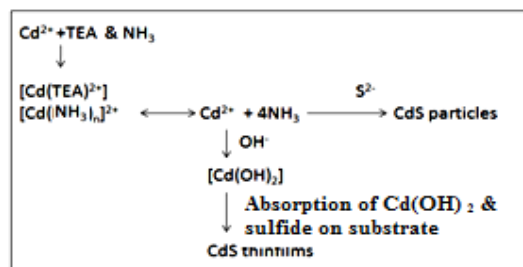
2.1 Sample Preparation

All the spectral pure chemicals are used in the present work. CdS thin films were synthesized by simple CBD dip coating techniques. Deionized (D.I) water, pure ammonia solution are used to control the pH value of the solution and triethanolamine (TEA) is used as a complexing agent, stabilizer (pH~13) respectively.

Primarily solution 1: cadmium and solution 2: sulfide was dissolved in deionized water and solution was stirred vigorously for 15 min to yield transparent and homogeneous solutions. Secondly ammonia solution was added to the solution to control the pH value of the solutions. TEA added in to the solution as a complexing agent. Later this solution was stirred continuously for an hour. Pure CdS, CdS with citric acid and CdS with tartaric

acid thin film samples are obtained and characterized by UV-Vis spectrometer, XRD, SEM and EDAX.

The schematic of the growth mechanism of pure CdS thin films by CBD is denoted by chemical equations for synthesizing pure CdS thin films as written below [2].



3. Results and discussion

3.1 Optical Properties

Absorption spectra of CdS thin films in the wavelength range 200 - 1100 nm are shown in Fig. 1(a). All the samples are having higher absorption values in the range from 200 – 450 nm and then gradually decrease up to 1100 nm. But CdS reacting with citric acids had sharp (high) absorption value than other samples in the wavelength range of 200 - 600 nm. The absorption peaks are shifted from red to blue region.

The absorption spectra of CdS thin films are decreased in positive range of short wavelength (< 350 nm) and increased above 350 nm. It also is considered that the positive might be due to the stoichiometry change of CdS resulting from the selective removal of sulfur by hydrogen [3].

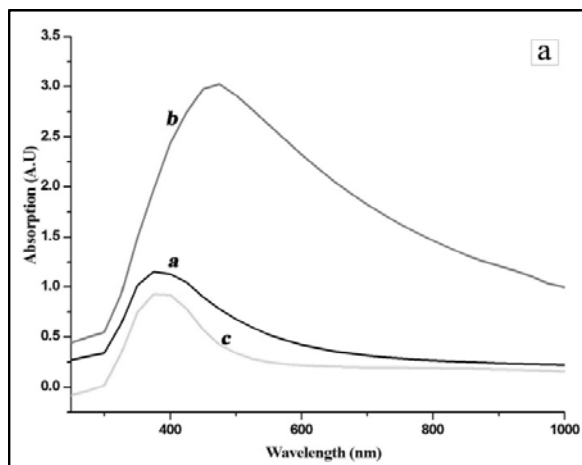


Fig. 1(a). Absorption spectra of films in the wavelength range 200 – 1100 nm. a, b and c lines are corresponding to pure CdS, CdS reacts with citric acids and CdS reacts with tartaric acid respectively

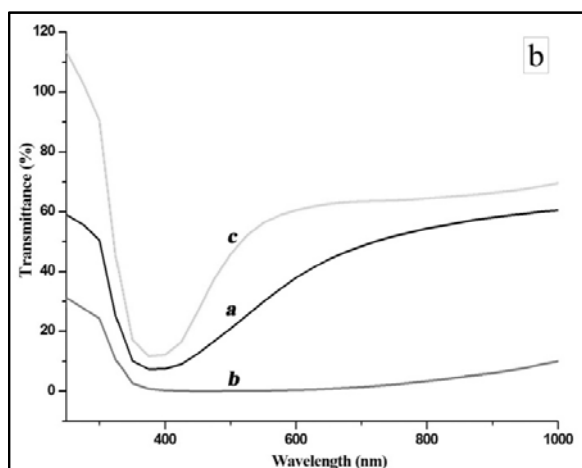


Fig. 1 (b). Transmittance spectra of films in the wavelength range 200 – 1100 nm. a, b and c lines are corresponding to pure CdS, CdS reacts with citric acids and CdS reacts with tartaric acid respectively

Transmittance spectra of thin films in the wavelength range 200 - 1100 nm are shown in Fig. 1(b), both pure CdS and CdS with citric acid are having increasing transmittance up to wavelength range from 800 – 1000 nm. CdS with tartaric acid are having increasing transmittance up to wavelength range from 400 - 1000 nm. The transmittance curve for all the samples are shifted towards blue to red region. The transmittance of CdS is in negative range of short wavelength (< 350 nm) and increased above 350 nm. It is considered that the negative might be due to the stoichiometry change of CdS resulting from the selective removal of sulfur by hydrogen [3].

3.2 Structural properties

The XRD analysis Fig. 2(a) shows that the pure CdS thin films have strong peaks at $2\theta = 10.50^\circ$, 48.14° and some minor peaks were also obtained at $2\theta = 31.48^\circ$, 48.32° , 52.67° etc. Fig. 2(b) shows that the CdS reacts with citric acids having the same strong peaks at $2\theta = 43.72^\circ$ and some minor peaks were obtained at $2\theta = 28.40^\circ$, 32.36° etc and Fig. 2(c) shows that the CdS when reacts with tartaric acids has some minor peaks at $2\theta = 38.39^\circ$, $2\theta = 48.78^\circ$ etc. From this analysis all the samples exhibit polycrystalline hexagonal and cubic CdS of random orientation which are known to show many strong X-ray diffraction peaks [4].

3.3 Crystallite size

Scherrer formula showed that the average dimension of the crystals that compose a crystallite size is related with the profile of the peak by means of the equation.

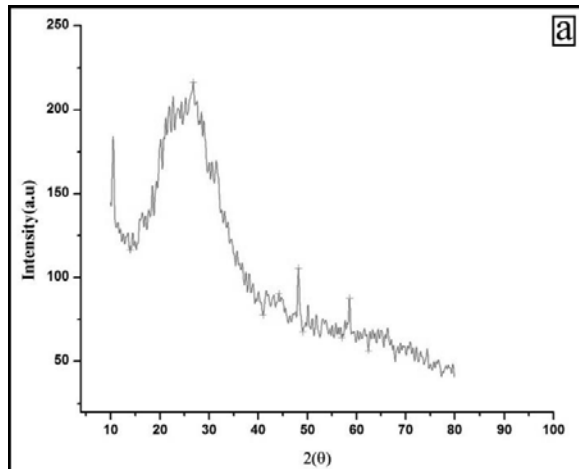
The crystallite size is calculated by Debye - Scherrer formula [5]

$$D = K \lambda / \beta \cos \theta \quad (1)$$

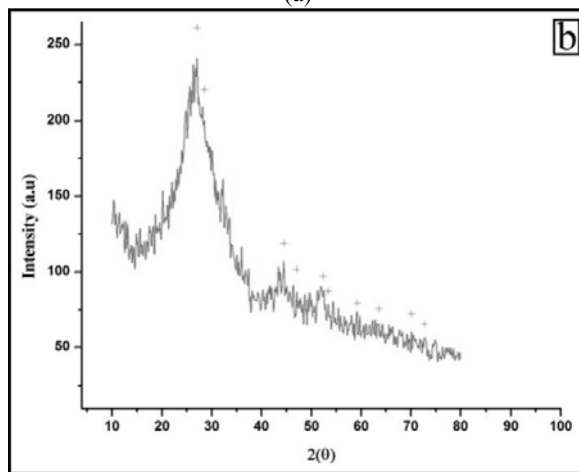
Here D is the crystallite size, λ is the wavelength of Cu K α radiation, θ is the Bragg angle, β is the Full width at half maximum (FWHM) of the peak in radians, K is proportionality constant approximately equal to unity and wavelength of the x-ray is 1.5406 Å (CuK α). The crystallite size is calculated for the pure (202.29 Å) CdS responds with citric acids (42.83 Å) and CdS reacts with tartaric acids (32.29 Å) respectively.

3.4 Surface analysis

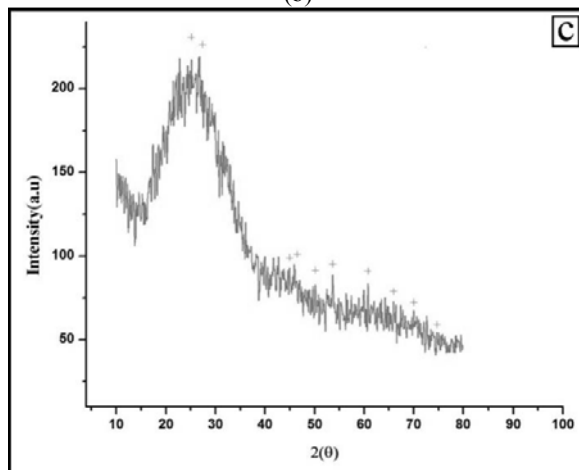
From the SEM images the Fig. 3(a) it is observed that the deposited thin films are not uniform throughout the region. But films are formed without any void, pin holes or cracks and that they cover overall substrates well. It is clearly observed that the small nanosize grain engaged is in a fibrous - like structure, which clearly indicates the crystallite nature along with some amorphous phase of CdS thin films [6]. The grain size is not uniform over all the substrate. The SEM image, Fig. 3(b) it is noticed that when CdS reacts with the citric acids, it improves the surface smoothness and also retains same structure. The crystalline size decreases due to CdS reacts with citric acids. The SEM image, Fig. 3(c) it is noticed that when CdS reacts with tartaric acids, it improves surface smoothness so that the results in the crystallite size are well decreased when compared with other two samples. As the crystallite size decreases, there is a blue shift of the absorption edge along with the oscillatory structure which is a signature of the size quantization effect [7-11].



(a)

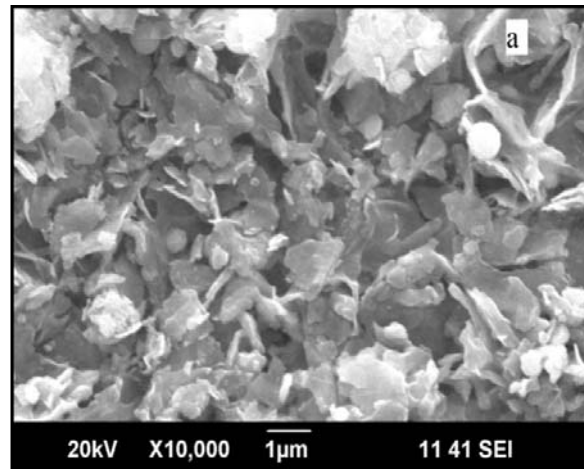


(b)

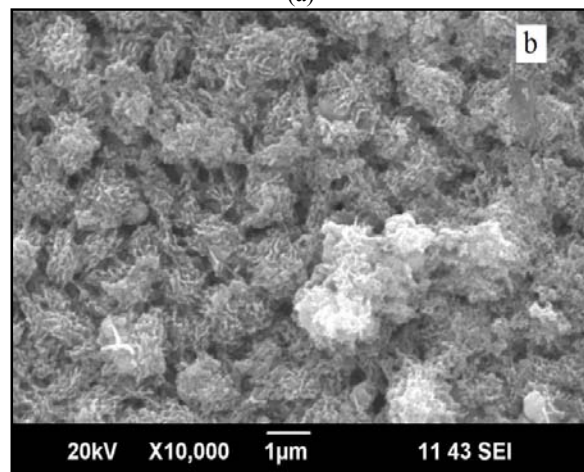


(c)

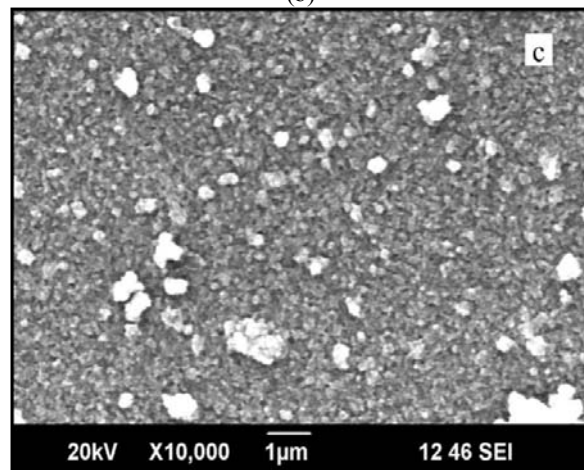
Fig. 2. XRD pattern of CdS films, (a) pure CdS, (b) CdS reacts with citric acids, (c) CdS reacts with tartaric acids.



(a)



(b)



(c)

Fig. 3. SEM micrographs of CdS thin films, (a) pure CdS, (b) CdS reacts with citric acids, (c) CdS reacts with tartaric acids.

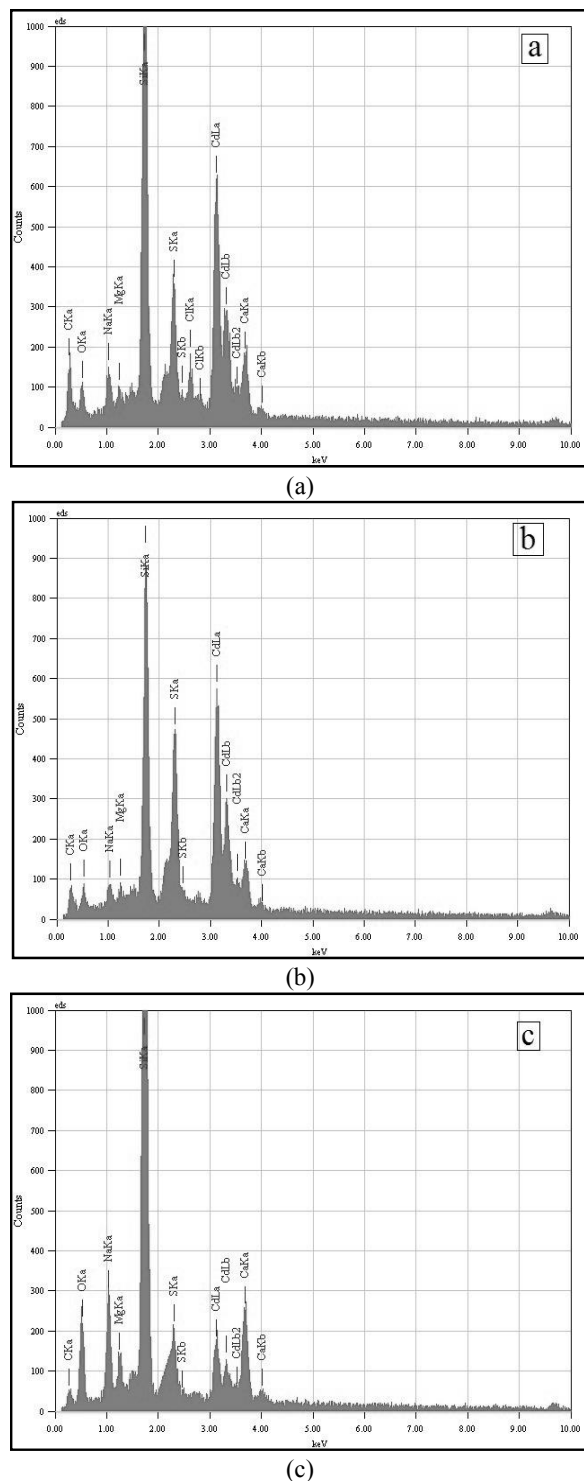


Fig. 4. EDAX spectra of CdS thin films: (a) pure CdS, (b) CdS reacts with citric acids, (c) CdS reacts with tartaric acids.

3.5 Compositions analysis

Quantitative energy dispersive x-ray analysis (EDAX) is the most commonly used investigation method, the grown crystal was subjected to EDAX analysis to conform the presence of elemental compositions by JEOL model (JED-2300 scanning electron microscope). It is confirmed that the cadmium (Cd) and sulfide (S) elements are presented in the deposited thin films as shown in the Fig. 4.

4. Conclusions

Effects of acids like (citric and tartaric acids) on structural, optical properties of CdS thin films were investigated. The transmittance of the CdS thin films was increased by tartaric acids up to 60–80 %, the absorption value of the CdS thin films were increased up to 60–90 % by citric acids, the crystallite size was decreased due to acidic content of citric and tartaric acids. SEM studies reveal that the surface smoothness was improved by acids like citric and tartaric acids compare with pure CdS thin films. The presence of elemental constituents was confirmed from EDAX analysis. CdS with citric acid films have highest absorption value when compared with others. These property makes the films suitable for optoelectronic devices for instance on layers.

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