

Characterization of nanocrystalline cadmium telluride thin films grown by successive ionic layer adsorption and reaction (SILAR) method

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Abstract. Structural, electrical and optical characteristics of CdTe thin films prepared by a chemical deposition method, successive ionic layer adsorption and reaction (SILAR), are described. For deposition of CdTe thin films, cadmium acetate was used as cationic and sodium tellurite as anionic precursor in aqueous medium. In this process hydrazine hydrate is used as reducing agent and NH_4OH as the catalytic for the decomposition of hydrazine. By conducting several trials optimization of the adsorption, reaction and rinsing time duration for CdTe thin film deposition was done. In this paper the structural, optical and electrical properties of CdTe film are reported. The XRD pattern shows that films are nanocrystalline in nature. The resistivity is found to be of the order of $4.11 \times 10^3 \Omega\text{-cm}$ at 523 K temperature with an activation energy of ~ 0.2 eV. The optical absorption studies show that films have direct band gap (1.41 eV).

Keywords. Thin film; CdTe; SILAR method.

1. Introduction

Thin films of CdTe are prepared by different chemical methods such as spray pyrolysis (Banerjee *et al* 1989), solution growth (Kuhaimi *et al* 2000), electro-deposition (Patil and Bhosale 2001) etc. In the present case, a simple chemical method, 'successive ionic layer adsorption and reaction (SILAR)' has been used to deposit CdTe thin films. The SILAR technique is relatively new and was first reported by Ristov *et al* (1985). The name SILAR was ascribed to this method by Nicolau (1985). In the SILAR technique, substrate is immersed into separate cation and anion precursor solutions and rinsed with purified water after each immersion (Nicolau and Menard 1988; Nicolau *et al* 1990). Nicolau used this method to grow polycrystalline and epitaxial thin films of water insoluble ionic or ion covalent compounds of the Cm An type of heterogeneous reactions at the solid-solution interface between adsorbed cations $[\text{CLp}]^{n+}$ and anions $[\text{AL'q}]^{m-}$, following the reaction:



where, Lp and L'q should be different ligands, but this is not a mandatory condition.

For preparation of CdTe thin films, sodium tellurite (Na_2TeO_3) is used as a Te source and cadmium acetate as a Cd source.

2. Experimental

This SILAR method does not require any expensive sophisticated instruments like vacuum system. It can be carried out in three glass beakers only, one containing a solution of a salt of the cation and another containing a solution of a salt of the anion and third containing rinsing water. In the present investigation, for preparation of CdTe thin films four-reaction vessels were used: vessel (1): 0.5 M cadmium acetate solution (80 ml), pH = 5, temperature 27°C; vessel (2): double distilled water; vessel (3): 0.4 M sodium tellurite solution (80 ml), 3 ml hydrazine hydrate, ammonia (NH_4OH) is added to adjust the pH (pH: 11), temperature 27°C and vessel (4): double distilled water.

One SILAR growth cycle involved following four steps: (i) substrate was immersed into cationic precursor (vessel 1) (0.5 M cadmium acetate solution) for 30 s, so the Cd^{2+} ions were adsorbed onto the substrate surface; (ii) then the substrate was rinsed with double distilled water for 30 s to remove loosely bonded Cd^{2+} ions from the substrate; (iii) further, the substrate was immersed into anionic precursor (vessel 3) (0.5 M sodium tellurite) for 30 s at 27°C so Te^{2-} ions were adsorbed and reacted with Cd^{2+} ions to form CdTe thin film and (iv) again the substrate was rinsed with double distilled water for 30 s to remove unadsorbed and unreacted Te^{2-} ions from the substrate.

Thus, one SILAR cycle had 30 s adsorption of cations, 30 s rinsing of cations, 30 s adsorption and reaction of anions and 30 s rinsing of anions.

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The film thickness was measured by using weight difference method. The thickness was measured by considering bulk density of CdTe (6.20 g/cm^3). The two-point d.c. probe method of dark electrical resistivity was used to study the variation of resistivity with temperature. The structural studies were carried out using Philips PW 1710 diffractometer, with Cu-K α radiation having wavelength, $\lambda = 1.5405 \text{ \AA}$. The optical characteristics were studied using Hitachi 330 spectrophotometer to find out the band gap energy.

3. Results and discussion

3.1 Reaction mechanism

CdTe thin films were grown on micro glass slide (size $72 \times 25 \times 1 \text{ mm}$), which were first cleaned in chromic acid, followed by repeated washing in deionized water. In the anions precursors solution, the sodium tellurite along with hydrazine as the reducing agent and NH_4OH (ammonia in water gives NH_4OH) as the catalytic was added for the decomposition of hydrazine and inhibition of the precipitation of tellurium compounds. Hydrazine supplies energy to reduce Te valency Te^{4+} to Te^{2-} , that creates a favourable condition for forming CdTe in the presence of Cd^{2+} ions at temperature, 60°C . The global reaction for the process is given as



It is worth mentioning that adding hydrazine hydrate to the solution improves the precipitation of CdTe on glass substrate.

3.2 Optimization of preparative parameters

The time duration for adsorption, reaction and rinsing was experimentally determined. Keeping concentration and immersion cycles constant, optimized immersion and rinsing time of deposition were determined. For such equivolumes of cadmium acetate and Na_2TeO_3 , hydrazine hydrate and NH_4OH of same concentrations (0.3 M) were taken. Numbers of deposited films were observed by conducting several trials, by changing immersion and rinsing time from 5–60 s. It was found that film attains the maximum thickness at immersion time of 30 s. Films deposited below this rinsing and immersion time are porous and not homogenous. Also growth rate decreases remarkably above this immersion and rinsing time. For optimization of concentration of cadmium ion source, equivolume of cationic precursor solution of cadmium acetate and anionic precursor solution of sodium tellurite

(0.4 M) along with NH_4OH were taken in separately placed beakers. By keeping number of immersion (900), immersion time (30 s), rinsing time (30 s) constant, the concentration of cationic precursor solution was varied from 0.05 – 0.6 M and respective thickness was measured and graph of thickness against concentration of cadmium chloride was plotted. Figure 1 shows variation of film thickness with cadmium ion concentration.

It was found that the CdTe film formation roughly starts from concentration (0.05 M) of cadmium acetate, when ionic product exceeds the solubility product and reaches a maximum value of thickness up to 0.5 M . At this concentration, average growth rate is maximum (0.31 nm/cycle). After 0.5 M concentration, the thickness goes on decreasing which may be due to formation of outer porous layer. Thus the optimized value of concentration is taken as 0.5 M . All these optimized conditions are reported in table 1.

3.3 XRD studies

Figure 2 shows XRD patterns of CdTe thin films by SILAR method. The patterns indicate that films are nanocrystalline in nature. The observed broad hump in XRD pattern is due to amorphous glass substrate. Comparison of d -values with ASTM data for CdTe (ASTM data file) shows that the material is CdTe having wurtzite (hexagonal) structure. CdTe film having thickness, 272 nm , shows four diffraction peaks at angles $2\theta \sim 24^\circ, 38^\circ, 65^\circ$ and 87° . They are associated with (002), (110), (211) and (220)

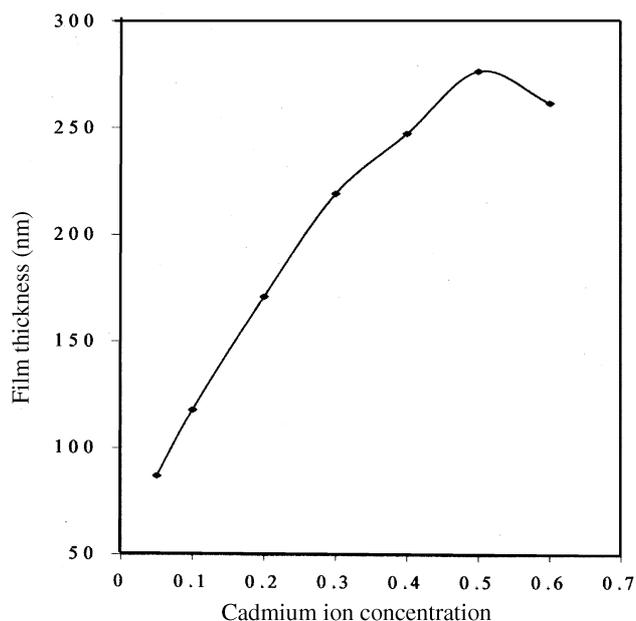
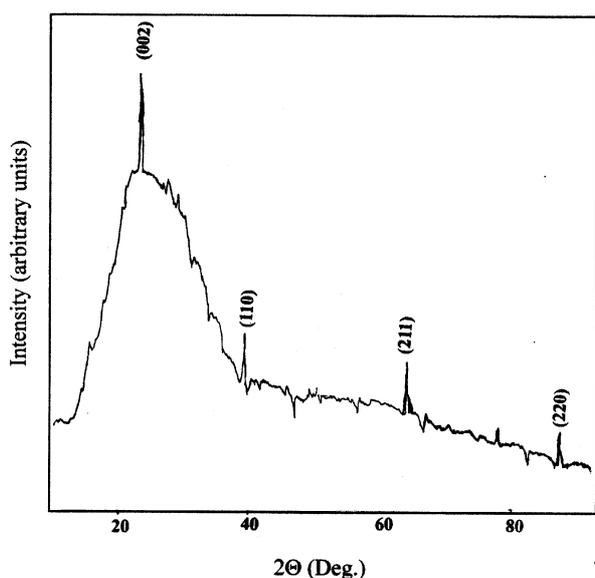


Figure 1. Variation of CdTe film thickness with cadmium ion concentration.

Table 1. Optimized conditions for the deposition of CdTe thin films.

Deposition conditions	Cationic precursor	Anionic precursor
Sources	Cadmium acetate	Sodium tellurite
Concentrations	0.5 M (CH ₃ COO) ₂ Cd (80 ml)	0.4 M Na ₂ TeO ₃ (80 ml) + hydrazine hydrate (4 ml) + NH ₃ (NH ₄ OH)
pH	5	11
Immersion time (s)	30	30
Rinsing time (s)	30	30
Immersion cycles	910	910
Temperature (°C)	27	27


Figure 2. X-ray diffraction pattern of CdTe thin film having thickness, 272 nm.

reflections of hexagonal (wurtzite) phase. These results are in good agreement with that obtained by Padam and Malhotra (1989).

The crystallite size was determined by using Scherrer formula,

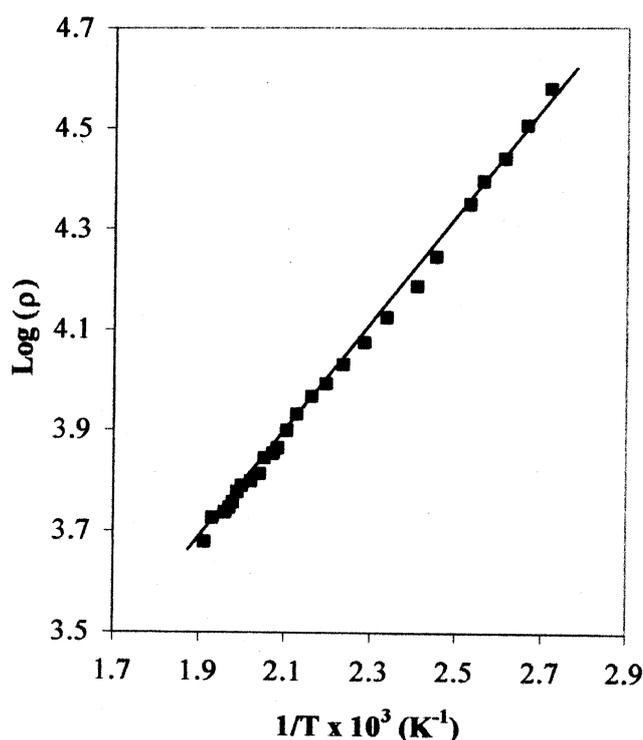
$$d = \frac{l}{b \cos q}, \quad (4)$$

where l is the wavelength used (1.54 Å), b the angular line width at half maximum intensity in radians and q the Bragg's angle.

Using Scherrer's formula, grain size was found to be of the order of 22 nm.

3.4 Studies of electrical resistivity

The electrical resistivity of CdTe films was studied in air. Figure 3 shows the variation of log of resistivity ($\log r$) with reciprocal of temperature ($1/T$) $\times 10^3$. It was seen that resistivity decreases with temperature indicating semiconducting nature of films.


Figure 3. Variation of $\log(r)$ vs $1/T \times 10^3$ (K⁻¹) for CdTe film having thickness, 272 nm.

The thermal activation energy was calculated using the relation,

$$r = r_0 \exp(E_0/KT), \quad (5)$$

where, r is resistivity at temperature T , r_0 a constant, K the Boltzmann constant (8.62×10^{-5} eV/K) and E_0 the activation energy required for conduction.

The activation energy was found to be of the order of ~ 0.215 eV for film having thickness, 272 nm. Several workers have reported the activation energy for CdTe thin films prepared by different methods, which is in good agreement with this result (Martin *et al* 1976; Ou *et al* 1984).

3.5 Optical absorption study

Optical absorption of CdTe thin films was studied in the wavelength range 450–1200 nm. Figure 4 shows the

variation of optical density (αt) with wavelength (λ) for the CdTe films having different thicknesses.

The nature of the transition (direct or indirect) is determined by using the relation

$$a = \frac{A(h\nu - E_g)^n}{h\nu}, \quad (6)$$

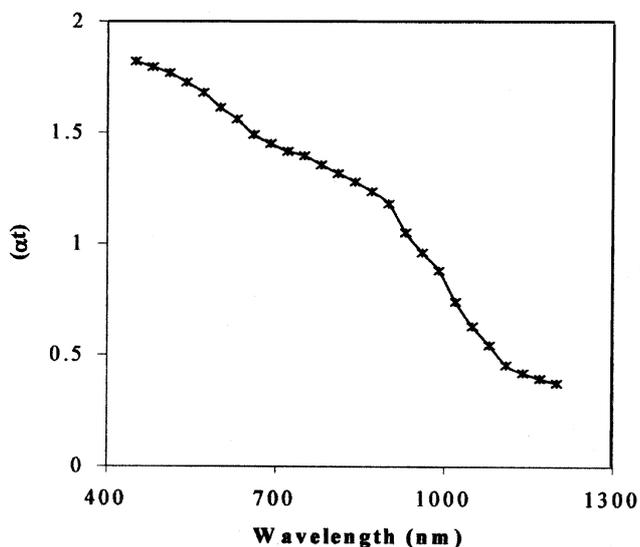


Figure 4. Plot of optical absorption (αt) vs wavelength for CdTe film of thickness, 272 nm.

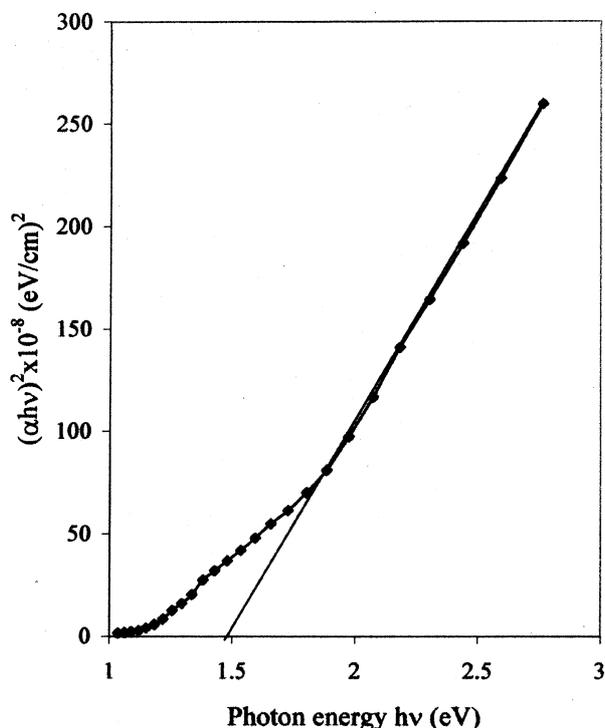


Figure 5. Plot of $(\alpha h\nu)^2$ vs $h\nu$ for CdTe film having thickness, 272 nm.

where $h\nu$ is the photon energy, E_g the band gap energy, A and n are constants.

For allowed direct transitions, $n = 1/2$ and for allowed indirect transitions, $n = 2$. The plot of $(\alpha h\nu)^2$ vs $h\nu$ is shown in figure 5 for CdTe films having thickness, 272 nm. Since the variation of $(\alpha h\nu)^2$ with $h\nu$ for CdTe films is a straight line indicating that the involved transition is direct one. Band gap energy, E_g , was determined by extrapolating the straight line portion to the energy axis for zero adsorption coefficient (α). The optical band gap energy was found to be 1.41 eV for film having thickness, 272 nm.

4. Conclusions

The successive ionic layer adsorption and reaction (SILAR) method was successfully used to deposit CdTe thin films from cadmium acetate and sodium tellurite as cationic precursor and anionic precursor. Under optimized conditions, films having thickness, 272 nm, were prepared in 910 SILAR deposition cycles. XRD studies show that films prepared by this method have hexagonal (wurtzite) structure. The electrical resistivity is of the order $4.11 \times 10^3 \Omega\text{-cm}$, at 523 K temperature; and it decreases with rise in temperature, which shows that films are semiconducting in nature. The study of optical absorption shows that band gap energy is 1.41 eV.

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