Studies on size dependent properties of cadmium telluride thin films deposited by using successive ionic layer adsorption and reaction method

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Successive ionic layer adsorption and reaction method (SILAR) have been used to deposit CdTe thin films onto glass substrate using cadmium chloride solution as cationic and sodium tellurite solution as anionic precursor. In order to study size dependent optical, structural and electrical properties, films having different thicknesses from 96 to 312 nm have been prepared by changing SILAR deposition cycles from 50 to 110. The XRD studies show that films were nanocrystalline in nature with Wurtzite (hexagonal) structure. A shift of band gap energy from 1.86 to 1.47 eV, a decrease in electrical resistivity from 10.52 × 10¹ to 4.78 × 10¹ Ω m (at 528 K), increase in grain size from 14.5 to 32.8 nm and decrease in activation energy from 0.39 to 0.19 eV have been observed when film thickness was varied from 96 to 312 nm. The films prepared are semiconducting in nature with p-type conductivity.

Keywords: Thin film growth, SILAR, Bandgap energy

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1 Introduction

Thin films are most promising for utilization in solar cells out of which cadmium chalcogenides have received intensive attention since their band gap lies close to the range of maximum theoretically attainable energy conversion efficiency¹. They can also be used in heterojunctions, IR detectors, llix meters, switching devices and Schottky barriers etc. The II-VI group compounds particularly CdTe, are attracting a lot of attention due to their potential application in producing photovoltaic devices and wide use in IR devices. Cadmium telluride is a semiconductor that has been considered attractive for use in solar energy conversion because of its suitable bandgap (E_g = 1.44 eV). Thin films of CdTe are prepared by variety of methods, such as, screen-printing², vacuum evaporation³, metal-organic chemical vapour deposition⁴, anodic and cathodic deposition⁵,⁶ and solution growth technique⁷. The polycrystalline CdTe films ⁸ have been prepared on glass and nickel substrate by flash evaporation and cathodic deposition technique. Some work has also been carried out on single crystal of CdTe⁹. CdTe epilayers grown by MOCVD¹⁰ and sputtering¹¹.

In the present investigation, we report the successful deposition of CdTe thin films by SILAR method. The chemical bath deposition technique in which deposition of metal chalcogenide semiconductor thin films occurs due to substrates maintained in contact with dilute chemical baths containing the metal and chalcogen ions. The film formation takes place when ionic product exceeds solubility product. This also results into precipitate formation into the solution and control over the process is lost. In order to avoid such difficulties, SILAR method was developed. It is based on the immersion of the substrate into separately placed cationic and anionic precursors and rinsing between every immersion with ion exchanged water to avoid homogeneous precipitation in solution. It is modified version of chemical bath deposition and may also be called as stepwise chemical deposition.

2 Experimental Details

The SILAR process involves three most important steps: (i) Specific adsorption of the most strongly adsorbed ions of the compound to be grown by substrate immersion in a solution of one of its salts, (ii) water rinsing of the excess solution still adhering to the substrate, and (iii) chemical reaction between the most strongly specifically adsorbed ions and the less strongly adsorbed ones by the subsequent substrate immersion in a solution containing the latter, entailing the growth.

In present work, CdCl₂ solution was used as cationic precursor and Na₂TeO₃ solution was used as anionic precursor.
The film thickness was measured by the method of weight difference. The thickness was obtained by assuming bulk density of CdTe (6.20 gm/cm³). The crystal structure and crystalline orientation of the films were determined with a Philips PW 1710 X-ray diffractometer using CuKα radiation (λ = 1.54 Å). The optical absorption spectra of the film were recorded on the UV-VIS-NIR spectrophotometer (Hitachi Model, 330, Japan).

3 Results and Discussion
3.1 Preparation of films
In the present case sodium tellurite solution was used along with hydrazine as the reducing agent and NH₃OH (ammonia in water gives NH₄OH) as the catalytic for the decomposition of hydrazine and inhibition of the precipitation of tellurium compounds. Hydrazine supplies energy to reduce Te valency Te⁴⁺ to Te²⁻ that a favourable condition is created for forming CdTe in the presence of Cd²⁺ ions. One SILAR growth cycle involves following four steps.

1) Immersion of substrate into cationic precursor (0.5 M CdCl₂ solution) for 30 seconds, so that Cd²⁺ ions are adsorbed onto the substrate surface,

2) Rinsing of the substrate with double distilled water for 30 seconds to remove loosely bonded Cd²⁺ ions from the substrate,

3) Immersion of the substrate into anionic precursor (0.5 M sodium tellurite + 0.5 NaOH + hydrazine hydrate + NH₃) for 30 seconds at 60°C so that Te²⁻ ions are adsorbed and react with Cd²⁺ ions to form CdTe thin film, and

4) The rinsing of substrate with double distilled water for 30 seconds to remove unadsorbed and unreacted Te²⁻ ions from the substrate.

The preparative parameters, such as, concentration, number of immersions, immersion time etc. are optimized to get good quality and well adhering CdTe thin films. In order to study thickness dependent properties, films having different thicknesses were prepared by changing number of deposition cycles. In single run 4-8 films were prepared having nearly same thickness. The films having different thicknesses were prepared by using optimized conditions of deposition as given in Table 1.

The number of immersion cycles is varied from 50 to 130. Figure 1 shows variation of film thickness with growth cycles. After 110 cycles, a maximum value of thickness of CdTe was obtained which may be called as terminal thickness. After 110 cycles, the thickness decreases due to peeling off the film from the substrate surface.

3.2 X-ray diffractometry
Figure 2 shows the XRD patterns of CdTe thin films grown by SILAR method. The pattern indicates that films are polycrystalline or nanocrystalline in nature. The observed broad hump in XRD patterns of all samples is due to amorphous glass substrate. Comparison of d-values with ASTM data for CdTe

| Table 1—Optimized conditions for the deposition of CdTe thin films |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | Cationic precursor | Anionic precursor | Concentrations (ml) | pH | Immersion time (s) | Rinsing time (s) | Immersion cycles | Temperature (°C) |
| Deposition conditions | Cadmium Chloride | Sodium Tellurite | 0.5 M CdCl₂ (70) | 5.0 to 5.2 | 30 | 30 | 30 | 60 |
| Anionic precursor | 0.4 M Na₂TeO₃ (70) + 0.5 M NaOH (5) + Hydrazine hydrate (4) + NH₃ (NH₄OH) | | | 11.0 to 11.2 | | | | |

Fig. 1—Thickness of SILAR grown CdTe thin films versus number of growth cycles
shows that material is CdTe having Wurtzite (hexagonal) structure. CdTe film having thickness 312 nm shows four diffraction peaks at angles 20~24°, 38°, 65° and 87°. They are associated with (002), (110), (211) and (220) reflections of hexagonal (Wurtzite) phase. These results are in good agreement with results, reported by few earlier workers\textsuperscript{17,18}. 

Comparison of XRD results with ASTM data is presented in Table 2 and a good agreement between the observed and the standard \(d\)-values is noticed.

The XRD pattern shows little crystallites. The crystallinity of the film was improved with thickness. The crystallite size was determined by using Scherrer formula

![X-ray diffraction patterns of CdTe thin film for different thickness. Film thickness: (A) 96 nm (B) 141 nm (C) 178 nm (D) 251 nm (E) 312 nm](image)

<table>
<thead>
<tr>
<th>Film thickness (nm)</th>
<th>Standard (d)-value (Å)</th>
<th>Observed (d)-value(Å)</th>
<th>Reflection plane (hkl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>3.75</td>
<td>3.735</td>
<td>(002)</td>
</tr>
<tr>
<td>141</td>
<td>3.75</td>
<td>3.762</td>
<td>(002)</td>
</tr>
<tr>
<td>178</td>
<td>2.295</td>
<td>2.236</td>
<td>(110)</td>
</tr>
<tr>
<td></td>
<td>1.462</td>
<td>1.437</td>
<td>(211)</td>
</tr>
<tr>
<td></td>
<td>3.75</td>
<td>3.791</td>
<td>(002)</td>
</tr>
<tr>
<td>251</td>
<td>2.295</td>
<td>2.262</td>
<td>(110)</td>
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<td></td>
<td>1.462</td>
<td>1.440</td>
<td>(211)</td>
</tr>
<tr>
<td></td>
<td>1.145</td>
<td>1.140</td>
<td>(200)</td>
</tr>
<tr>
<td>312</td>
<td>2.295</td>
<td>2.284</td>
<td>(110)</td>
</tr>
<tr>
<td></td>
<td>1.462</td>
<td>1.458</td>
<td>(211)</td>
</tr>
<tr>
<td></td>
<td>1.145</td>
<td>1.138</td>
<td>(200)</td>
</tr>
</tbody>
</table>
Where $\lambda$ is the wavelength used (1.54 Å), $\beta$ is the angular line width at half maximum intensity in radians and $\theta$ is the Bragg’s angle.

To determine grain size of the CdTe particles by considering a common plane (200), slow scan between the angle (22.5°) and (25.5°) was carried out with a step of 0.02° (2$\theta$) per minute for the film having different thicknesses. Using Scherrer’s formula, grain size was calculated as given in Table 3.

### 3.3 Electrical resistivity

The electrical resistivity of CdTe films was studied in air. Figure 4 shows the variation of log of resistivity ($\log \rho$) with reciprocal of temperature ($1/T \times 10^3$).

For all the films it was seen that resistivity decreases with temperature indicating semiconducting nature of films. Resistivity of CdTe film decreases from $10.72 \times 10^1$ to $4.78 \times 10^1$ Ω m as film thickness increases from 96 to 312 nm at temperature 523 K.

This decrease in resistivity is due to the improvement in crystallinity of the films (grain size increased from 14.5 to 32.8 nm), as the film thickness was increased from 96 to 312 nm. The thermal activation energies for different films were calculated using the relation,

$$\rho = \rho_0 \exp \left( \frac{E_0}{k_B T} \right), \quad \ldots (2)$$

where, $\rho$ is resistivity at temperature $T$, $\rho_0$, a constant, $k_B$, Boltzmann constant ($8.62 \times 10^{-5}$ eV/K), and $E_0$ is the activation energy required for conduction.

Figure 4 shows variation of activation energy with CdTe film thickness. Activation energies are of the order of 0.39 to 0.195 eV as the film thickness was increased from 96 to 312 nm. Activation energy for CdTe thin films prepared by different methods is reported by several workers$^{19-21}$ which is ~ 0.2 eV, which may be due to presence of a shallow impurity level at 0.2 eV above the valence band.

### 3.4 Thermoelectric power

In measurement of thermoelectric power it is found that voltage developed across the junction changes from 6.1 to 12.5 mV as CdTe film thickness changes from 96 to 312 nm. The temperature difference between the ends of sample causes transport of
carriers from hot to cold end and thus creates electric field, which gives thermal voltage. The dependence of thermo e.m.f. on temperature is shown in Fig. 5. The plots show increase in magnitude of thermo e.m.f. with thickness, which may be due to the decrease in electrical resistivity of film with thickness variation from 96 to 312 nm. From polarity of thermo e.m.f, p-type conductivity of CdTe thin films was confirmed. Same nature of conductivity of CdTe thin films was reported earlier\textsuperscript{22,23}.

3.5 Optical absorption

Optical absorption of CdTe thin films was studied in the wavelength range 450 to 1200 nm. Figure 6 shows the variation of optical density (\(\alpha t\)) with wavelength (\(\lambda\)) for the CdTe films having different thickness. The nature of the transition (direct or indirect) is determined by using the relation

\[
\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad \ldots (3)
\]

where, \(h\nu\) is the photon energy, \(E_g\), the band gap energy and \(A\) and \(n\) are constants. For allowed direct transitions \(n = 1/2\) and for allowed indirect transitions \(n = 2\).
4 Conclusion

It is concluded that band gap energy of CdTe decreases from 1.86 to 1.47 eV as the film thickness is increased from 96 to 312 nm and grain size from 14.5 to 32.8 nm. Similar results\textsuperscript{24} have been reported for ZnO, PbS and GaAs materials. A decrease in electrical resistivity from $10.52 \times 10^3$ to $4.78 \times 10^3$ $\Omega$ cm (at 528 k), increase in grain size from 14.5 to 32.8 nm and decrease in activation energy from 0.39 to 0.19 eV were observed when film thickness was varied from 96 to 312 nm. The films prepared by this SILAR method show $p$-type conductivity.

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References