Compositional, structural, optical and electrical properties of solution grown CdTe thin films

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CdTe films were prepared by solution growth technique. Influence of the preparation technique on compositional, structural, optical and electrical properties of polycrystalline CdTe films was investigated using energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmission and electrical resistivity. EDS analysis shows that CdTe films are nearly stoichiometric. X-ray studies show that as grown films are composed of zinc blende and wurtzite structure. The films predominately show wurtzite structure. Optical measurements indicate the existence of one direct allowed optical transition with a corresponding energy gap of 1.46 eV. The optical parameters (n, k, α) were evaluated by simple straight forward calculations using the transmission spectrum. The electrical resistivity of solution grown CdTe films was found to be $2.5 \times 10^6$ Ωm for film grown on glass substrate and $5 \Omega m$ for film grown on Ag substrates. The lateral result is attributed to the effect of grain boundary, crystal size, the degree of preferred orientation, internal micro-strain and stoichiometry of the film.

1 Introduction

CdTe and its ternaries cadmium zinc telluride and cadmium mercury telluride are some of the most important materials today for quantum defect studies\textsuperscript{1} in which future generation are based on photovoltaic (PV) device. Additionally, CdTe is one of large band gap II-VI semiconductors that can be either p- or n-type. Based on the defect modes, an excess of Cd produces n-type CdTe, an excess of Te results in p-type CdTe. Conductivity can also\textsuperscript{2} be altered by the presence of impurities\textsuperscript{3,4}. Most of the problems associated with the use of p-type CdTe films are attributed to self-compensation and the difficulty of forming stable and low resistance ohmic contacts.

The knowledge of optical, electrical and structural properties of CdTe films is very important in many scientific, technological, and industrial applications in the field of optoelectronic devices, particularly solar cells. A broad variety of deposition techniques\textsuperscript{5-14} permits the deposition of CdTe with desirable optical, electrical and structural properties. These include close space sublimation (CSS), close space vapour transport (CSVVT), screen printing (SP), electro-deposition (ED) and chemical bath deposition (CBD).\textsuperscript{5,14} Chemical solution growth is relatively inexpensive, simple and convenient in particular for large area deposition, therefore in the present work compositional, structural, optical and electrical properties of CBD CdTe films have been made using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), optical transmission and electrical resistivity measurements.

2 Experimental Details

2.1 Sample preparation

CdTe thin films were grown on micro glass slide, glass/tin oxide, Cu, Ag, Al and Si wafers, which were first cleaned in chromic acid, followed by repeated washing in deionized water. Once cleaned, the substrates were mounted vertically in a beaker containing a deposition mixture maintained at a temperature of 90-95°C. The deposition mixture contained $1.0 \times 10^{-2}$ M CdAc and $1.0 \times 10^{-3}$ M TeO\textsubscript{2}. The later was brought into solution in NaOH, the pH being adjusted to $\sim 2$ by addition of 10% H\textsubscript{2}SO\textsubscript{4}. CdTe films were deposited on various kinds of substrates according the following reaction:

\[
\text{HTeO}_2^+ + 3\text{H}^+ + 4e^- \rightarrow \text{Te} + 2\text{H}_2\text{O}
\]
\[
\text{Cd}^{2+} + \text{Te} + 2e^- \rightarrow \text{CdTe}
\]

It is worth mentioning that adding hydrazin hydrated to the solution improve the precipitation of CdTe on Si, microglass and glass/tin oxide.

The beaker containing the slides and the deposition mixture was vigorously stirred magnetically during
deposition. After 30-60 min, the slides were removed, washed with deionized water to remove loosely bound CdTe powder, and finally cleaned ultrasonically. In some instances, multilayers of CdTe film were deposited by repeating the above process.

2.2 Compositional studies

The composition of the films was determined by EDS (JSM-5800), which allows image observation and elemental analysis to be performed efficiently. Fig. 1 shows EDS spectra for CdTe film grown on Ag substrate.

2.3. Structural studies

X-ray diffractometer (Phillips PW1700) with Ni-filtered CuKα-radiation was used to study the structural properties of the films. Fig. 2 shows X-ray diffraction patterns of CdTe films deposited on Ag, Cu, Al, Si, glass/SnO₂, and glass substrates. The JSM-5800 SEM was used to study the micro-structural properties of the films.

2.4 Spectrophotometric measurements

The spectral distributions of transmission T were measured in the spectral range of 700-2000 nm. Measurements of T were carried out at normal incidence at room temperature using Zeiss spectrophotometer.

2.5 Electrical measurements

Two-probe method was used for resistivity measurements. The electrical resistivity was measured using 619C Keithley electrometer and direct current source. The specific contact resistivity is defined as

\[ \rho_c = \frac{I}{(\delta J/\delta V)_{V=0}} = \frac{A}{R_{\text{contact}}} \text{ohm-m}^2 \]

where \((\delta J/\delta V)_{V=0}\) is the slope of the J-V curve at zero bias, \(A\) is the contact area and \(R_c\) is the resistance of the contact. This definition of contact resistivity is used throughout this paper and serves as the major basis of comparison between contacts.

3 Results and Discussions

Films of varying thickness in the range 0.5-2 μm were grown on Ag, Cu, Al, glass/SnO₂, and silicon substrates. Composition of CdTe films was determined by EDS analysis. The results of EDS analysis are presented in Table 1. The elemental analysis of the sample investigated of this work is expressed in atomic percent. Fig 1 illustrated EDS spectra for typical CdTe films grown on Ag substrate. CdTe films grown on Ag, Cu, glass, glass/SnO₂, and silicon show an excess of Te while CdTe films grown on Al show an excess of Cd. Te rich film always produces p-type material, while Cd rich film always produce n-type material. One factor that appears to be important is the formation of Te rich surface layer, which appears to lower the barrier at the semiconductor-metal interface for Te thickness greater than about 5 nm.

The crystallographic properties have been investigated by X-ray diffraction technique using CuKα radiation. CdTe exists in two crystalline modifications: the hexagonal (Wurtzite) phase and the cubic (zincblende) phase. CdTe films deposited on glass show very simple spectra, while films deposited on glass/SnO₂, Ag, Cu, Al and Si show many diffraction peaks, associated with both cubic and hexagonal phases. CdTe films grown on glass substrate show single diffraction peak at 2θ = 26.5°.

![Fig. 1 — EDS spectra for CdTe film grown on Ag](image)

Table 1 — EDS analysis of CdTe films

<table>
<thead>
<tr>
<th>Substrate material</th>
<th>Te%</th>
<th>Cd%</th>
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<tbody>
<tr>
<td>Al</td>
<td>57.81</td>
<td>42.19</td>
</tr>
<tr>
<td>Cu</td>
<td>58.51</td>
<td>41.49</td>
</tr>
<tr>
<td>Ag</td>
<td>57.1</td>
<td>42.9</td>
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</table>
Fig. 2 — X-ray diffraction pattern for solution grown CdTe films

(Fig. 2), indicating a strong preferred orientation. This peak could be associated with (002) reflection of hexagonal CdTe or the (111) reflection of the cubic modification. The preferred orientation of the CdTe films is due to controlled nucleation process associated with the low formation rate of CdTe. CdTe film grown on glass/SnO₂ substrate shows a preferred orientation at 2θ = 26.5° and four additional diffraction peaks at 34°, 37.75°, 51.5° and 65.5°. They are associated with the (102), (110), (202) and (211) reflections of the hexagonal modification or the (111), (220) and (331) reflections of the cubic modification. CdTe films grown on Si shows five diffraction peaks at 38°, 41°, 46°, 56° and 71°. They are associated with the (110), (103), (112), and (300) reflections of the hexagonal modification or (220), (311) and (422) reflections of the cubic modification. CdTe films grown on Ag substrate shows six diffraction peaks at 26.5°, 32°, 38°, 43°, 45° and 65°. They are associated with the (002), (102), (110), (103), (112) and (211) reflections of the hexagonal modification or the (111), (220), (311) and (331) reflections of the cubic modification. CdTe film grown on Cu substrate shows five diffraction peaks at 24°, 43°, 46°, 56° and 71°. They are associated with the (002),
(103), (112), (202) and (300) reflections of the hexagonal modification or the (111), (311) and (422) reflections of the cubic modification. CdTe film grown on Al substrate shows five peaks at 32°, 37°, 45°, 65.5°, and 79°. They are associated with the (102), (110), (112), (211) and (205) reflections of the hexagonal modification or (220), (311), (331) and (511) reflections of the cubic modification. The wurtzite (hexagonal) is a predominant structure for CdTe films deposited on various kinds of substrates. These results are in good agreement with that obtained by Padam and Malhotra. The inter-planar spacing d_{klh} were found from Bragg's law, \( 2d \sin \theta = \lambda \), where \( \theta \) is the diffraction angle, \( \lambda \) is the incident wavelength. d(A) values of all the films were calculated and compared with the standard d values given in ASTM card data file 19-770 for zinc blende and 19-193 for the wurtzite.

The results are presented in Table 2 and a good agreement between the observed and the standard d-values is noticed.

The crystallite size (CS) was determined using the Scherrer formula:

\[
CS = \frac{K \lambda}{\beta \cos \theta}
\]

where the constant \( K \) is a shape factor usually = 1, and \( \beta \) the corrected full width at the half maximum (FWHM). Table 2 represents the crystallite size of CdTe film grown on different substrates calculated from the (002) reflection. The crystallite size is measured in the direction normal to the reflection plane, i.e. in the <002> direction, and consequently perpendicular to the substrate. Therefore, the increase in the crystallite size may be interpreted in terms of a columnar growth. Large crystalline sizes were obtained for film grown on Ag, Cu and Al substrates.

Fig. 3 shows a scanning electron micrographs of CdTe films grown on both Ag and glass substrates. It is clear from the micrographs that film grown on Ag substrate has a larger grain size than that grown on glass substrates. It is evident from the micrographs that the

<table>
<thead>
<tr>
<th>2θ</th>
<th>Glass</th>
<th>Glass/SiO₂</th>
<th>Cu</th>
<th>Al</th>
<th>Ag</th>
<th>Si</th>
<th>Wurtzite</th>
<th>Cubic</th>
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<tbody>
<tr>
<td>24</td>
<td>3.71</td>
<td>3.71</td>
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<td>111</td>
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<td>-</td>
<td>2.79</td>
<td>2.79</td>
<td>-</td>
<td>102</td>
<td>-</td>
</tr>
<tr>
<td>37-38</td>
<td>-</td>
<td>2.3</td>
<td>-</td>
<td>2.36</td>
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<td>110</td>
<td>220</td>
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<td>-</td>
<td>2.1</td>
<td>2.15</td>
<td>-</td>
<td>103</td>
<td>-</td>
</tr>
<tr>
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<td>2.01</td>
<td>2.01</td>
<td>1.97</td>
<td>-</td>
<td>112</td>
<td>311</td>
</tr>
<tr>
<td>54</td>
<td>1.75</td>
<td>1.79</td>
<td>-</td>
<td>-</td>
<td>1.72</td>
<td>-</td>
<td>202</td>
<td>-</td>
</tr>
<tr>
<td>65-65.5</td>
<td>-</td>
<td>1.42</td>
<td>-</td>
<td>1.42</td>
<td>1.43</td>
<td>-</td>
<td>211</td>
<td>331</td>
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<tr>
<td>71</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.32</td>
<td>-</td>
<td>300</td>
<td>422</td>
</tr>
<tr>
<td>78-79</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>205</td>
<td>511</td>
</tr>
</tbody>
</table>

Fig. 3 — Scanning electron micrograph of CdTe film grown on (a) Ag and (b) glass.
structure of the film grown on Ag substrate is in the form of spherical grains while CdTe film grown on glass substrate is in the form of tilted inverted pyramids.

The optical band gap energies were obtained from the plot of \( (\alpha h \nu)^2 \) (\( \alpha \) is the absorption coefficient) versus photon energy \( (h \nu) \) in the wavelength range 700-2000 nm. As shown in Fig. 4 the values of the optical band gaps are determined by extrapolating the linear part of CdTe film indicating the existence of one direct allowed optical transition corresponding to 1.46 eV.

Knowing the experimental transmittance \( T_{exp} \) and film thickness \( t \) of a given CdTe thin film, the refractive index \( n \) and the absorption index \( k \) of this film were calculated using the method described by Swanepoel. The refractive index \( n(\lambda) \) and absorption index \( k(\lambda) \) as a function of the wavelength are illustrated in Fig. 5. From this figure the following conclusions can be drawn:

The discrepancy of either \( n \) and \( k \) lies within the limits of the experimental error.

The extinction coefficient values and the refractive index values are partially independent of the method of preparation.

The dark resistivity of CdTe films was measured at room temperature using a two-probe technique. The electrical resistivity of the CdTe films grown on various substrates are given in Table 3. It is clear that the resistivity of the films grown on metal substrates is smaller than that grown on glass, glass/SnO\(_2\) and Si substrates. Ag, Cu and Al substrates also serve as a back contact of CdTe based solar cells. Low resistance contacts are essential for the production of highly efficient solar cells. Thus for one major problem encountered with promising \( p \)-CdTe based solar cells, such as CdS/CdTe, ZnO/CdTe and ITO/CdTe, has been the lack of suitable contact. Although the formation of low resistance contacts to semiconductors tend to be more an art than a science, a careful investigation to contact mechanisms is needed for specific problem area like \( p \)-type CdTe. In the present work, the authors give attention to metal contacts which are known to act as acceptors in CdTe, like Cu and Ag. It is evident from Table 1 that Ag/CdTe film is nearly stoichiometric. Fig. 2 shows XRD patterns for solution grown CdTe films. When XRD pattern of Ag/CdTe film compared with that of Cu/AgTe film, it can be observed that the predominant peak (for Ag/CdTe film) occurs at 20 = 65° (d = 1.43Å) indicating a preferred orientation, this peak could be associated with (211) reflection of hexagonal CdTe or (331) reflection of the cubic modification, while the

![Fig. 5 — Refractive index and coefficient versus wavelength for CdTe film](image)

| Table 3 — Values of resistivity \( \rho \) and crystallite size (CS) of CdTe films |
|---------|-------|-----------------|-------------|--------|
| Substrate material | \( \rho \) | Type of conductivity | Contact resistivity | CS (nm) |
| Ag      | 0.5   | \( p \)-type      | \( 0.12 \times 10^{-2} \) | 17.98   |
| Cu      | 0.8   | \( p \)-type      | \( 1.2 \times 10^{-2} \) | 17.98   |
| Al      | 1.2   | \( n \)-type      | \( 2.4 \times 10^{-2} \) |        |
| Si      | \( 3.5 \times 10^{2} \) | \( p \)-type |        | 9       |
| glass/SnO\(_2\) | \( 2.9 \times 10^{6} \) | \( p \)-type |        | 3       |
| glass   | \( 2.5 \times 10^{8} \) | \( p \)-type |        | 3       |
predominant peak (for Cu/CdTe film) occurs at $2\theta = 54^\circ$ ($d = 1.79 \text{Å}$) indicating a preferred orientation, this peak is associated with (202) reflection of hexagonal modification. Fig. 3 shows SEMs of CdTe films. It is evident from the micrographs that substrate material influence the growth of the film. It can be observed that Ag/CdTe film has larger grain.

The best contact found in this investigation was Ag as shown in Table 3. This is attributed to the effect of grain size, the degree of preferred orientation, internal micro-strain and stoichiometry of the film.

4 Conclusions

P-type CdTe thin films have been successfully prepared by solution growth technique. The influence of preparation technique on the compositional, structural, optical and electrical properties have been investigated. The films predominantly show a wurtzite structure. Optical measurements indicate a direct band gap of 1.46 eV. Electrical resistivity indicates that the resistivity decrease for CdTe films deposited on Ag, Cu and Al substrates.

References