Electron transport mechanisms in CdS\textsubscript{x}Te\textsubscript{1-x} solid solution thin films prepared by thermal evaporation method

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Abstract. In this paper, CdS\textsubscript{x}Te\textsubscript{1-x} (0≤x≤1.0) thin films were prepared by thermal evaporation method in vacuum. X-ray diffraction (XRD) revealed that the films exhibited a zincblende structure with the preferred orientation of (111) plane when x ≤ 0.2. However, when x ≥ 0.8, they had a wurtzite structure with the preferred orientation of (002) plane. For the composition 0.2 ≤ x ≤ 0.6, the zincblende and wurtzite phases coexisted in the system and the films became less preferentially oriented. Atomic force microscopy (AFM) was used to study the morphological features of the samples. Energy gap values in the range of 1.45-2.39 eV were deduced from optical transmission spectra. The temperature dependence of electrical conductivity from room temperature down to liquid-helium temperature of CdS\textsubscript{x}Te\textsubscript{1-x} thin films was performed in order to identify the dominant conduction mechanism. It was shown that three types of conduction mechanisms can be expected. In the high temperature range about 220-300 K, Seto’s model of thermionic emission dominated, whereas, in the low temperature range (about 145-185 K), the dominant hopping conduction was Mott variable range hopping. However, the lower temperature region (about 70-105 K) Efros-Shklovskii variable range hopping was observed. The set of parameters describing the properties of localized electrons in each conduction behavior were examined.

1. Introduction

In the past years CdS/CdTe heterostructure has been regarded as one of the most promising structure for high efficiency and low cost solar cells. Theoretical calculations suggest a maximum efficiency around 30 % while the report efficiency is around 22.1% [1]. Light absorption and charge separation in CdTe thin film solar cells largely occur in the vicinity of the CdS/CdTe interface [2]. An interdiffusion process taking place at the CdS-CdTe interface during the cell production has been pointed out as one of the efficiency limiting factors through the resulting change in the band gap [3]. Thus, it is important to have a full understanding of the optoelectronic properties of such ternary compound CdS\textsubscript{x}Te\textsubscript{1-x}. The films of CdS\textsubscript{x}Te\textsubscript{1-x} were prepared by variety of methods, such as close spaced sublimation, magnetron sputtering, chemical bath deposition, spray pyrolysis and thermal evaporation methods. In this study, we prepared CdS\textsubscript{x}Te\textsubscript{1-x} thin films of the whole range of composition (x) by a single source thermal evaporation in vacuum. The crystal structure of the films
was analyzed by XRD. Surface morphology was observed by AFM. The energy gap values of the films were evaluated from the optical transmission spectra. Electrical conduction mechanisms of all the films were investigated at the temperature down from 300 to 20 K. We have studied these solid solution ternary thin films in order to improve the performance of CdS/CdTe solar cell.

2. Materials and methods
Cadmium sulfo telluride (CdS$_x$Te$_{1-x}$) thin films deposited on slide glass substrates by a single source thermal evaporation in vacuum of $5\times10^{-5}$ mbar by keeping the substrate temperature at 100°C. CdS and CdTe starting materials with 99.999% purity were purchased from Sigma-Aldrich. The starting materials were weighed regarding to the stoichiometric composition, further mixed and ground together; then pressed in a pellet form with a pressure about 6 GPa for using as the precursor for thermal evaporation in vacuum. The as-deposited films were annealed at 200°C for 30 min in a stream of slowly flowing pure N$_2$ gas. The crystal structure of these films was checked by X-ray diffraction technique with a Brucker D 8 diffractometer using CuK$_\alpha$ radiation. The crystallite size (L) was calculated using Scherrer’s formula, neglecting peak broadening due to residual stresses in the films, 

$$L = \frac{0.9\lambda}{\beta\cos\theta}$$

where $\beta$ is the broadening of diffraction line measured at half its maximum intensity in radian and $\lambda$ is the wavelength of X-rays (0.1540 nm). Surface morphology was examined by Park XE-100 AFM. Optical transmission measurements were performed with UV-Vis-NIR LAMDA 750 spectrophotometer in the wavelength range of 350-2500 nm. The temperature-dependent conductivity of CdS$_x$Te$_{1-x}$ thin films was measured by two probe method. Two silver electrodes with area 0.05 cm$^2$ were fabricated on the sample surface. The cryogenic system with a He closed cycle allows us to measure electrical conductivity of the films from 300 to 20 K using a cryostat model RDK 10-320 supplied by Leybold vacuum.

3. Results and discussion

3.1 Structural analysis
Figure 1 shows XRD patterns of CdS$_x$Te$_{1-x}$ thin films deposited on slide glass substrates by a single source thermal evaporation. For $x<0.2$, XRD revealed that CdS$_x$Te$_{1-x}$ thin films exhibited a zincblende structure with the preferred orientation of (111) plane. However, for $x \geq 0.8$, the films existed in the wurtzite structure with the preferred orientation of (002) plane. For the composition $0.2 \leq x \leq 0.6$, the zincblende and the wurtzite phases coexisted in the system and the films became less preferentially oriented. The coexistence of the zincblende and wurtzite phases often occurring in films with composition $(x)$ in the range 0.2-0.8 has been previously reported [4-8]. With increasing composition $(x)$, the strongest peak intensity shifted to a higher 2θ value; this is due to the partial replacement of Te atoms by S atoms. Figure 2 shows AFM images of the films of different compositions. AFM images of the films with composition $x = 0$ showed a polycrystalline character with pyramidal shaped crystallites, typical of cubic crystallites oriented in (111) plane. The grain size increased from 105 nm to 260 nm, as the value of $x$ increased from 0 to 1. As composition $(x)$ increased up to 0.4, the coexistence of flattening and pyramidal shaped crystallites was observed; this was consistent with the mixed phases seen in the XRD results. Then, a well-defined prism geometry was observed when $x=1$. The surface roughness decreased from 5.10 nm (for $x = 0$) to 3.12 nm (for $x = 0.4$), and then increased to 6.43 nm (for $x=1$).
3.2 Optical properties

Figure 3 shows the optical transmission spectra of CdS$_x$Te$_{1-x}$ thin films in the wavelength range of 350-2500 nm. The value of energy gap is given by the intercept of the straight line with the energy axis. Figure 4 shows the plots of $(\alpha h \nu)^2$ vs. $h \nu$ of the films with different compositions approximated a straight line, indicating that the optical transition in the films corresponded to the model for direct allowed transition. The value of the energy gap value is given by the intercept of the straight line with the energy axis. Energy gap values were found to be 1.51, 1.47, 1.45, 1.54, 2.00, 2.39 eV corresponding to composition $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$, respectively.
3.3 Electrical properties

The variation of electrical conductivity of the films with composition (x) at room temperature is shown in Figure 5. The lowest conductivity value about $1.6 \times 10^{-9} \left( \Omega \cdot cm \right)^{-1}$ was observed in the films with $x=0.6$. However, the highest conductivity value around $4.5 \times 10^{-3} \left( \Omega \cdot cm \right)^{-1}$ as obtained in the films with $x=0.8$. Normally, CdS films exhibit n-type semiconductor while CdTe films exhibit p-type semiconductor. From the thermoelectric test, the films with $x \leq 0.4$ show p-type, but the films with $x \geq 0.6$ show n-type. Our results are in good agreement with the earlier report [9]. The conductivity type started to change from p-type to n-type when $x$ reached 0.6. It indicated that the amount of charge carrier between the electrons and holes is approximately the same order or refute.

The Arrhenius plot of $\ln(\sigma)$ vs. $\frac{1000}{T}$ of CdS$_x$Te$_{1-x}$ thin films for the whole composition (0≤$x$≤1.0) are shown in Figure 6.

![Figure 3. Transmission spectra of CdS$_x$Te$_{1-x}$ thin films.](image)

![Figure 4. (αhν)$^2$ vs. hν plot of CdS$_x$Te$_{1-x}$ thin films.](image)

![Figure 5. Variation of conductivity with composition (x) of CdS$_x$Te$_{1-x}$ thin films at 300 K.](image)

![Figure 6. ln(σ) vs. 1000/T plot of CdS$_x$Te$_{1-x}$ thin films.](image)

Figure 7 (a) shows the plot of $\ln(\sigma)$ and 1000/T for the films with $x=0.8$. Two regimes are observed in the curve. At high temperature, $\ln\sigma$ exhibits an Arrhenius like behavior, while notably deviates from it at lower temperature. For high temperature range, the electrical conductivity of the sample is dominated by thermal activation passing through grain boundaries. The temperature dependence of the
electrical conductivity of the films was firstly analyzed using Seto’s model as the following relation [10]:

\[
\ln(\sigma T^{1/2}) = -\frac{E_a}{k} \left( \frac{1}{T} \right) + \ln \sigma_0
\]  

where \( \sigma_0 \) is pre-exponential factor, \( k \) is Boltzmann’s constant and \( E_a \) is the activation energy. This model related to grain boundaries which trap carriers and the barrier height value appeared. As shown in Figure 7 (b), a good linear relationship can be observed in the Arrhenius plot in the high temperature range (220-300 K). The important parameters deduced from Seto’s model were listed in Table 1: \( L \) is crystallite size, \( E_b \) is barrier height, \( N_d \) is donor concentration, \( E_t \) is trap energy level, \( N_t \) is trap concentration, \( L_D \) is Debye length and \( \varepsilon_r \) is dielectric constant taken from the literature [11].

Figure 7 (c) shows the plot of \( \ln(\sigma T^{1/2}) \) vs \( T^{-1/4} \). The plot was found to be linear at temperature range of 145-185 K. This suggested that the conduction is controlled by Mott variable-range hopping (Mott-VRH) instead of the Seto’s model at high temperature. The Mott’s parameters can be extracted from the relation [12]:

\[
\ln(\sigma T^{1/2}) = -\left( \frac{T_{0,Mott}}{T} \right)^{1/4} + \ln \sigma_{0,Mott}
\]  

The important parameters deduced from Mott-VRH model were tabulated in Table 2: \( T_{0,Mott} \) is a characteristic temperature coefficient, \( \sigma_{0,Mott} \) is pre-exponential factor, \( N(E_F) \) is density of state at the Fermi level, \( R_{hop,Mott} \) is average hopping distance, and \( W_{hop,Mott} \) is average hopping energy. At very low temperature range (70-105K), the measured data were satisfied the Efros-Shklovskii variable-range hopping (ES-VRH). In this electrical conduction mechanism region, the electron interaction caused the density of state at Fermi level is separated and became to the coulomb gap (\( \Delta_c \)). The conductivity in ES-VRH model is given as [13]

\[
\ln(\sigma T) = -\left( \frac{T_{0,ES}}{T} \right)^{1/2} + \ln \sigma_{0,ES}
\]  

Figure 7 (d) shows the plot of \( \ln(\sigma T) \) vs \( T^{-1/2} \). The important parameters deduced from ES-VRH model were listed in Table 3: \( T_{0,ES} \) is a characteristic temperature coefficient, \( \sigma_{0,ES} \) is pre-exponential factor, \( R_{hop,ES} \) is average distance, \( \xi_{ES} \) is localization length and \( W_{hop,ES} \) is average hopping energy.
Figure 7. (a) ln(σ) vs 1000/T plot, (b) ln(σT^{1/2}) vs 1000/T plot, (c) ln(σT^{1/2}) vs T^{-1/4} plot and (d) ln(σT) vs T^{-1/2} plot of CdS_{x}Te_{1−x} thin films for x=0.8.

Table 1. Seto’s parameters at high temperature of CdS_{x}Te_{1−x} thin films for x=0.8.

| Composition (x) | E_g (eV) | ε_r | L (nm) | E_b (meV) | N_d (cm^{-3}) | E_F (eV) | N_I (10^{11} cm^{-2}) | L_D |
|----------------|---------|-----|--------|-----------|---------------|---------|----------------|------|
| 0.0            | 1.51    | 12.62 | 77.7   | 59.9      | 4.18×10^{16}  | 0.694   | 3.20            | 16.53 |
| 0.2            | 1.47    | 12.24 | 39.9   | 13.5      | 3.50×10^{16}  | 0.721   | 1.41            | 17.81 |
| 0.4            | 1.45    | 11.74 | 15.1   | 17.3      | 3.16×10^{17}  | 0.703   | 4.77            | 5.95  |
| 0.6            | 1.54    | 11.51 | 3.4    | 23.5      | 1.45×10^{18}  | 0.746   | 28.72           | 1.15  |
| 0.8            | 2.00    | 11.13 | 5.9    | 12.9      | 8.54×10^{18}  | 0.907   | 9.09            | 2.69  |
| 1.0            | 2.39    | 10.56 | 34.2   | 25.4      | 9.0×10^{16}   | 1.174   | 3.08            | 11.24 |

Table 2. Mott’s parameters at low temperature of CdS_{x}Te_{1−x} thin films for x=0.8.

| Composition (x) | σ_{0,Mott} (Ω⋅cm)^{-1} | T_{0,Mott} (K) | N(E_F) (cm^{-3}⋅eV^{-1}) | R_{hop,Mott} (nm) | R_{hop,Mott} / ε_{Mott} (Ω⋅cm)^{-1} | W_{hop,Mott} (meV) |
|----------------|------------------------|----------------|--------------------------|-------------------|--------------------------------------|-------------------|
| 0.0            | 1.57×10^{-3}           | 5.58×10^{6}   | 9.69×10^{19}             | 3.81              | 4.72                                 | 110.49            |
| 0.2            | 2.21×10^{-5}           | 5.44×10^{6}   | 6.44×10^{22}             | 0.85              | 1.05                                 | 42.91             |
| 0.4            | 4.90×10^{-3}           | 5.13×10^{3}   | 8.73×10^{22}             | 0.74              | 0.92                                 | 36.85             |
| 0.6            | 2.75×10^{-7}           | 1.21×10^{4}   | 1.98×10^{22}             | 1.03              | 1.28                                 | 77.48             |
| 0.8            | 4.34×10^{-1}           | 4.57×10^{3}   | 8.84×10^{22}             | 0.79              | 0.91                                 | 36.64             |
| 1.0            | 6.01×10^{-3}           | 3.65×10^{4}   | 2.92×10^{21}             | 1.66              | 2.06                                 | 104.23            |

Table 3. ES’s parameters at very low temperature of CdS_{x}Te_{1−x} thin films for x=0.8.

| Composition (x) | σ_{0,ES} (Ω⋅cm)^{-1} | T_{0,ES} (10^{3} K) | R_{hop,ES} (nm) | ε_{ES} (nm) | R_{hop,ES} / ε_{ES} (Ω⋅cm)^{-1} | W_{hop,ES} (meV) | ΔC (µeV) |
|----------------|----------------------|-------------------|----------------|-------------|---------------------------------|-----------------|----------|
| 0.0            | 1.57×10^{-3}         | 5.58×10^{6}       | 9.69×10^{19}   | 3.81        | 4.72                            | 110.49          |          |
| 0.2            | 2.21×10^{-5}         | 5.44×10^{6}       | 6.44×10^{22}   | 0.85        | 1.05                            | 42.91           |          |
| 0.4            | 4.90×10^{-3}         | 5.13×10^{3}       | 8.73×10^{22}   | 0.74        | 0.92                            | 36.85           |          |
| 0.6            | 2.75×10^{-7}         | 1.21×10^{4}       | 1.98×10^{22}   | 1.03        | 1.28                            | 77.48           |          |
| 0.8            | 4.34×10^{-1}         | 4.57×10^{3}       | 8.84×10^{22}   | 0.79        | 0.91                            | 36.64           |          |
| 1.0            | 6.01×10^{-3}         | 3.65×10^{4}       | 2.92×10^{21}   | 1.66        | 2.06                            | 104.23          |          |
4. Conclusions

CdS$_{x}$Te$_{1-x}$ thin films in the entire range (0≤$x$≤1.0) were prepared by vacuum thermal evaporation method on glass substrate using mixed powders of CdS and CdTe compounds. From XRD results, CdTe-like phase belonging to zincblende phase was observed when $x \leq 0.2$. In contrast, CdS-like phase belonging to wurtzite structure was obtained when $x \geq 0.8$. For the composition 0.2 ≤ $x$ ≤ 0.6, the zincblende and wurtzite phases coexisted in the system and the films became less preferentially oriented. The crystallite size in the range 105-260 nm was elucidated by AFM. The optical transition on CdS$_{x}$Te$_{1-x}$ thin films was found to be direct allowed transition type. The variation of energy gap value with composition ($x$) in the range of 1.45-2.39 eV was observed. From the thermoelectric test, the conductivity type started to change from p-type to n-type when composition ($x$) reached $x=0.6$ due to auto-compensation of charge carrier between the electrons and holes. The temperature range of 20-300 K, it was shown that three types of electrical conduction mechanisms can be expected. In the high temperature range (>220 K), thermionic emission across grain boundary dominates, whereas in the low temperature range (145-185 K) the dominant hopping conduction is Mott’s variable range hopping. At very low temperature range (70-105 K), the Efros-Shklovskii variable-range hopping is observed. The films with $x=0.8$ showed the highest conductivity and also high energy gap value which may suitable to solar cell application.

5. References

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\hline
\textit{x} & 0.0 & 0.2 & 0.4 & 0.6 & 0.8 & 1.0 \\
\hline
\textit{Eg} (eV) & 4.31\times10^{-7} & 4.31\times10^{-7} & 6.15\times10^{-7} & 6.15\times10^{-7} & 6.15\times10^{-7} & 6.15\times10^{-7} \\
\textit{Tc} (K) & 9.01 & 3.51 & 4.53 & 4.05 & 3.45 & 3.37 \\
\textit{C} (J/K mol) & 48.12 & 77.03 & 67.81 & 71.72 & 77.64 & 112.03 \\
\textit{S} (J/K mol) & 64.13 & 164.04 & 127.38 & 142.87 & 167.73 & 171.14 \\
\textit{K} (J/K mol) & 0.75 & 0.47 & 0.53 & 0.50 & 0.46 & 0.65 \\
\textit{\sigma} (S/cm) & 12.90 & 8.16 & 9.18 & 8.69 & 8.02 & 5.59 \\
\textit{\rho} (ohm cm) & 1.28 & 20.6 & 27.2 & 12.3 & 23.9 & 4.29 \\
\hline
\end{tabular}

\textit{(@100 K)}