Annealing temperature dependence of properties of CdSe thin films by RF-sputtering

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Abstract. Cadmium Selenide (CdSe) is a II-VI group compound semiconducting material with a direct band gap about 1.74 eV, which is widely applied in thin film transistors, light emitting diodes and photoelectrochemical (PEC) cells. In recent years, the application of CdSe thin films to CdTe thin film solar cells has attracted the attention of people. CdSe thin films were synthesized using radio frequency magnetron sputtering method on Corning glass substrates at room temperature. The as-deposited films were annealed at various temperatures (200°C, 300°C, 400°C and 500°C) in N₂ atmosphere for 1h and the effect of annealing temperature on structural, morphological, compositional, optical and electrical properties was studied. X-ray diffraction (XRD) indicates that the structure of CdSe thin films transforms from cubic to hexagonal structure when annealing temperature changes from room temperature to 500°C. Scanning electron microscope (SEM) images show that the crystallite size of CdSe thin films has no obvious increase with annealing temperature increasing from 200°C to 400°C, which is all about 33 nm. However, grains with size of 200 nm were precipitated on the surface of CdSe thin film annealed at 500°C, and the Se content of CdSe thin film decreased. The band gaps of CdSe thin films were found to firstly decrease, and then gradually increase with the increase of annealing temperature. The minimal band gap of CdSe thin film is 1.63 eV when annealed at 300°C. The conductivity of CdSe thin film annealed at 500°C increased by two orders of magnitude compared with as-deposited CdSe thin film.

Keywords: CdSe thin films; annealing temperature; RF-sputtering

1. Introduction
CdSe thin films have been well applied in numerous fields such as thin film transistors[1, 2], light emitting diodes [3, 4] photoelectrochemical (PEC) cells [5] and solar cells [6-9]. In recent few years, CdSe thin films were used as window or absorption layers in CdTe solar cells, whose short circuit current density greatly improved [7-9]. Annealing has a great influence on the optical and electrical properties of the CdSe film [10-13]. So it is necessary to study the annealing of CdSe thin film. CdSe is a II-VI semiconductor material with a direct band gap (~ 1.74 eV), which is suitable for visible light spectrum in the solar spectrum and has a strong photoelectric effect when excited by visible light. CdSe thin films have been prepared using different methods such as chemical bath deposition (CBD) [11, 12], electrodeposition [13], thermal evaporation method [14], radio frequency (RF) magnetron sputtering [7] and pulsed laser deposition (PLD) [8]. CdSe thin film deposited by RF magnetron sputtering is compact and of greatly crystalline. The thickness of CdSe thin films is accurately controlled by changing sputtering power, sputtering pressure, and gas flow.

Annealing treatment provides great versatility for the preparation of CdSe thin films with tunable...
size, band gap, and surface appearance. Annealing in different atmosphere of CdSe thin films deposited by different methods have been widely reported. Nair et al have reported that an annealing process can enhance the photosensitivity of chemically deposited CdSe thin films [10]. The effect of annealing on structural, optical, and electrical properties of CdSe thin films deposited by CBD method was investigated by Kale et al [11]. They have reported that the structure of CdSe thin films changed from cubic to hexagonal phase with the decrease in value of band gap from 2.3 to 1.7 eV after annealing [15, 16]. The electrical resistivity of CdSe thin films was found in the order 10^2–10^6 Ω cm which was observed decrease after annealing. Erat et al have reported the influence of annealing in nitrogen atmosphere and its dependency on structural, compositional, and electrical properties of chemical bath deposited CdSe thin films [12]. They found that the Se content in the film decreased gradually and activation energy became smaller with the increase of annealing temperature. A study on the effect of annealing on structural, optical, morphological and electrical properties of thermally evaporated CdSe thin films was reported by Purohit et al [14]. They have reported that the CdSe thin films have cubic phase with preferred orientation (111) and the surface morphology and roughness improved after annealing process. Somnath and Asit have reported the effect of annealing on structural, optical and photosensitive properties of electrodeposited CdSe thin films [13]. They have showed that the sensitivity of CdSe thin films increases with annealing temperature increasing from room temperature to 350°C and then decreases.

An attempt has been made in this paper to enhance optical and electrical properties of CdSe thin films deposited by RF-sputtering. In this work, CdSe thin films were deposited by RF magnetron sputtering at room temperature, and the as-deposited films were annealed at various temperatures (200 °C, 300 °C, 400°C and 500 °C) in N2 atmosphere for 1h and the effect of annealing on structural, morphological, compositional, optical and electrical properties was studied.

2. Experimental

2.1 Preparation
CdSe thin films have been deposited on corning glass substrates by RF magnetron sputtering. Substrates were cleaned in the deionized water for 10min and then cleaned in anhydrous ethyl alcohol for 5min assisted by ultra-sonic and, finally, they were dried in a drying oven before deposition. The CdSe target material (Chengdu Ultra-pure Application Materials Limited Liabilities Company) is more than 99.99% pure. The chamber was initially evacuated to a pressure of 8.0×10^-4 Pa and the 99.999% pure argon was then introduced using a mass flow meters with the flow rate of 50 sccm to maintain the chamber pressure at 2.0Pa. CdSe thin films were sputtered for 2h with a 100W RF power at room temperature. The thicknesses of as-deposited CdSe thin films are about 440nm. The as-deposited films were annealed at 200°C, 300°C, 400°C and 500°C in nitrogen atmosphere for 1h in vacuum annealing furnace and followed by normal cooling to room temperature.

2.2 Characterization
The thickness of as-deposited and annealed CdSe thin films was measured with a step profiler (XP-2, Ambios Technology Inc. USA). The structure of CdSe thin films was characterized by X-ray diffraction (XRD, DX-2600 Dandong Fangyuan Instrument Co. Ltd., China) system with the Cu Kα radiation (λ=0.15406 nm) and the 2θ range between 10° and 70°. The Surface morphology and composition of CdSe thin films were studied using a scanning electron microscope (SEM, Hitachi S-4800) and dispersive X-ray spectroscopy (EDS, INCA, Inca Oxford) attached with the same SEM system respectively. The optical transmission spectra were measured in the wavelength range of 300–2500nm with a UV–Vis–NIR grating spectrophotometer (Perkin-Elmer Lambda 950). The electrical resistivity of CdSe thin films in dark was performed using two-probe method in the temperature range 300-573K.

3. Results and discussion
3.1 Structure, morphology and composition

Figure 1(a) shows the XRD pattern of as-deposited CdSe thin film deposited by RF sputtering which is crystalline with cubic sphalerite structure. The intense peak at 25.65° corresponding to the plane (111) suggests a dominant orientation of nanocrystalline phase of CdSe thin film with cubic zinc blende structure (PDF standard card, JCPDS 88-2346). The CdSe thin films deposited by CBD [17, 18], thermal evaporation [14] and electrodeposition [19] respectively at room temperature have been reported to be cubic zinc blende structure.

![Figure 1](image_url)

Figure 1. XRD patterns of CdSe thin films with different annealing temperature: (a) As-deposited, (b) 200℃, (c) 300℃, (d) 400℃, (e) 500℃.

Figure 1(b)-(e) show the XRD patterns of annealed CdSe thin films. The increase of peak intensity at (111) indicates that the film has been converted to a stable cubic phase with better crystallinity after annealed at 200℃ [figure 1(b)]. In figure 1(c), the waning of the highest peak intensity and appearance of peak at (101) indicated the structure of CdSe thin film gradually changed from cubic to hexagonal phase. CdSe thin film annealed at 300℃ was polycrystalline with a mixture cubic and hexagonal structure. Further, with the increase of annealing temperature (400℃-500℃), the highest peak intensity at (002) in figure 1(d)-(e) gradually strengthened and the peak at (101) and (103) are observed. The results indicated that CdSe thin film has a stable hexagonal phase with (002) preferential orientation after annealed at 500℃ (PDF standard card, JCPDS 77-2307). The especial peak at 33.12°corresponding to (002) plane (PDF standard card, JCPDS 75-0594) indicates that the part of CdSe phase was converted to CdO phase resulting from the accidental incorporation of oxygen. The crystallite size of CdSe thin films was calculated from Scherrer’s formula [13]. Calculation results show that average crystallite sizes of CdSe thin films except for film annealed at 500℃ vary from 31.9 nm to 34.3 nm. The grain size of CdSe thin film annealed at 500℃ was too large to be calculated by Scherrer’s formula, which was estimated to be about 200nm by SEM [figure 2(e)].

The surface morphology of as-deposited and annealed CdSe thin films is showed in figure 2(a)-(e). In figure 2(a), it is observed that the as-deposited thin film was flat and dense with homogeneous distribution of sphere-like particles. With the increase of annealing temperature [figure 2(b)-(d)], the grain sizes of CdSe thin films have varied slightly, which were all about 33nm estimated by SEM. The result is well agreement with the results by XRD. But there are some obvious cracks appearing on the thin films. The appearance of cracks is attributed to the expansion of the original cracks with thermal annealing and the change in volume caused by transformation from cubic to hexagonal phase. From figure 2(a)-(d), it can be see that the surface of films is smoother with the increase of annealing temperature, and the connections between grains are tighter. This is the result of grain consolidation.
with thermal annealing. A drastic change in surface morphology is observed for 100°C increase in annealing temperature with respect to figure 2(e). The area of rectangle in figure 2(e) shows the ball-like particle precipitates out on the surface of the film. These ball-like particles gradually grew and agglomerated together, and formed the single crystal like pyramid (the area of circle in figure 2(e)). There were similar reports in the research of Shyju [17] and Somnath [13]. Excellent single crystalline structures of size as big as 200nm with clear crystallographic faces are noticed to evolve on the surface of film.

Figure 2. SEM of CdSe thin films with different annealing temperature: (a) As-deposited, (b) 200°C, (c) 300°C, (d) 400°C, (e) 500°C.

Energy-dispersive analysis by X-rays has been carried out to study the stoichiometry of as-deposited and annealed CdSe thin films. The average atomic percentage of Cd:Se was 50.61:49.39 showing the chemical composition of the sample is nearly 1:1 for the as-deposited CdSe film by RF-sputtering. The average atomic percentage of Se was slightly higher than Cd for the film of annealed at 300°C. A small amount of compositional variation is attributed to the rearrangement of atoms with thermal annealing [17]. The average atomic percentage of Cd:Se was 57.91:42.09 for film annealed at 500°C showing Se content decreased significantly, owing to evaporation of selenium from thin film with thermal annealing [12]. The deficiency of selenium content leads to cadmium-rich of CdSe thin film, making cadmium to dedicate electrons as a donor. In this way, the strengthening of n-type conduction of the film is beneficial to the formation of p-n junction in solar cells.

3.2 optical properties

The transmission spectra of as-deposited and annealed samples are illustrated in figure 3. Compared with CdSe thin films obtained by CBD [12] and electrodeposited [13], the CdSe thin films deposited by RF-sputtering have high transmittance, which can reach over 90%. Such CdSe thin film with high transmittance can be well applied to the window layer of the thin film solar cell, thereby increasing the short-circuit current density of solar cell. The interference fringe pattern in the near infrared (NIR) region owes to the constructive and destructive interference of the wave fronts from two interfaces air/CdSe film and CdSe film/corning substrate [20]. With thermal annealing, the sharper absorption edge varying between 700 nm and 800 nm indicates that the crystallization of films is getting better.

Absorption coefficient $\alpha$ can be obtained by a relation of $\alpha = -1/d\ln T$ at the absorption edge where $d$ is the film thickness and $T$ is the transmittance[21]. The transmission data were analyzed to calculating the gap energies of CdSe thin films by using the following relation $\alpha = \left(\frac{k}{\hbar \nu}\right)(\hbar \nu - E_g)^n$ where $\alpha$ is absorption co-efficient, $\hbar \nu$ is the photon energy, $k$ is a constant, $E_g$ is the optical band gap and $n$ equals 1/2 and 2 for direct and indirect allowed transitions respectively[15]. The band gap energy of as-deposited and annealed CdSe thin film has been determined by the plot of $(\alpha \hbar \nu)^2$ versus $\hbar \nu$ based on the above formula as shown in figure 4.

Figure 4 showed band gaps with the increase of annealing temperature for CdSe thin films. The band gaps were found to firstly decrease slightly, and then gradually increase with thermal annealing. The minimal band gap of CdSe film is 1.641eV when CdSe film annealed at 300°C, which is favorable to apply CdSe thin film for CdTe solar cell as absorption layer. Due to the quantum size effect, the band gaps decreases gradually with the increase of grain sizes [20]. But in our study, there isn’t large change in the $E_g$ values for the thin films annealed at 200°C-300°C, owing to the small
difference in the grain size obtained by SEM and XRD studies. It is interesting to note that the band gaps increased significantly for the thin films annealed at 400°C-500°C. There are two possible reasons for the increase of the band gaps: i) The increase of the band gaps may be attributed to a shift in stoichiometry which is encountered in the work of Mondal et al[22], ii) we can see the film annealed at 500 °C with the emergence of the single crystal from the SEM images above[figure 2(e)], and the value of band gap is found to be 1.7 eV for annealed films at 500 °C, which is quite closer to the value reported earlier for CdSe single crystal [23].

![Figure 3. Optical transmittance spectra of as-deposited and annealed CdSe thin films.](image)

![Figure 4. Tauc plots and band gaps with annealing temperature for as-deposited and annealed CdSe thin films.](image)

### 3.3 Electrical properties

The electrical resistivity of as-deposited CdSe thin films and CdSe thin films annealed at 500°C in dark was performed using two-probe method in the temperature range 300-573K. The resistivity of CdSe thin films decreases with the increase of annealing temperature, confirming semiconducting behavior of CdSe thin films [11]. The resistances of the films annealed at 200°C, 300°C and 400°C are too large to be measured. When the temperature rises to 433K, the resistivity of as-deposited film was measured to be 3.4×10^4 Ω cm. The high value of resistivity of as-deposited film can be due to the dislocation, crystallite boundary discontinuities and presence of surface state. It is observed that the resistivity of the film after annealing decreased by two orders of magnitude compared with the as-deposited film in table 1. The decrease of resistivity may be attributed to the growth of grains, the decrease of defects and increase of carrier concentration (The deficiency of selenium content leads to cadmium-rich of CdSe thin film annealed at 500°C, and equivalents to increasing the donor impurity, thus the carrier concentration is increased.).

| Samples         | electrical resistivity ρ(Ω cm) | activation energy Ea(eV) |
|-----------------|-------------------------------|--------------------------|
|                 | 325K                          | 433K                     | 548K                     |
| As-deposited    | None                          | 3.4×10^4                 | 5.7×10^2                | 0.733                    |
| Annealed at 500°C | 5.3×10^4                  | 7.0×10^2                 | 3.5                     | 0.712                    |

The activation energies of dark conductivity of thin films were calculated by using the following relation $\rho = \rho_0 e^{\frac{E_a}{kT}}$ where $\rho$ is the resistivity at temperature $T$, $\rho_0$ is a constant, $k$ is Boltzman constant [11]. The calculated activation energies in 410K-480K of as-deposited CdSe thin films and CdSe thin films annealed at 500°C are 0.733eV and 0.712eV, respectively.

### 4. Conclusion

The effect of annealing temperature on the properties of CdSe thin films by RF-sputtering was studied.
The structure of CdSe thin films gradually transforms from cubic to hexagonal phase, and the crystallite sizes were maintained at around 33nm with the increase of annealing temperature (≤400°C). However, when the annealing temperature reached 500°C, the surface morphology of CdSe thin film changed significantly, and grains with size of 200 nm were precipitated on the surface of CdSe thin film. The Se/Cd ratio changed from 49.39:50.61 for as-deposited CdSe thin film to 42.90:57.91 for CdSe thin film annealed at 500°C. CdSe thin films maintained high transmittance after annealing. The band gaps of CdSe films firstly decrease, and then gradually increase with the increase of annealing temperature. The minimal band gap of CdSe thin film is 1.63eV when annealed at 300°C. The conductivity of CdSe thin film increased by two orders of magnitude after annealed at 500°C. The calculated activation energies in 410K-480K of CdSe thin films as-deposited and annealed at 500°C are 0.733eV and 0.712eV, respectively. These results are of great reference value for the development of CdSe thin film with high conductivity and high transparence and its application to optoelectronic devices.

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6. Reference
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