Thermally and Optical-Induced Effect on Optical and Electrical Parameters of Ag-Doped CdSe Thin Films

Jagdish Kaur · S. K. Tripathi

Received: 15 July 2014/Revised: 15 November 2014/Published online: 15 February 2015
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2015

Abstract Thin films of Ag-doped CdSe are deposited on the glass substrates by thermal evaporation technique using inert gas condensation method. The elemental composition of the prepared thin film is confirmed by EDX spectra. SEM analysis reveals the uniform distribution of the grains over the substrate. TEM analysis reveals the spherical nature of nanoparticles having size in the range of 25–30 nm. X-ray diffraction study indicates an increase in the grain size after thermal annealing and the decrease in the grain size after light soaking treatment. Transmittance spectra are found to decrease with corresponding red shift after annealing and light soaking of as-deposited thin films. The value of the band gap is found to decrease and refractive index increases, after annealing and light soaking treatment. The dispersion of refractive index is described using the Wemple–DiDomenico single oscillator model and the effects of the annealing and the light soaking on the dispersion parameters are studied. The dark conductivity is found to change from 2.24×10^{-8} to 1.54×10^{-7} and $1.45 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ after annealing and light soaking of thin films, respectively. Hall effect measurement reveals n-type behavior of as-deposited, annealed and light-soaked thin films.

KEY WORDS: CdSe; Thin film; Surface treatment; Electrical properties

1 Introduction

Semiconducting nanomaterials are the building block of the nanodevices such as photovoltaic devices [1], electronic devices [2], light-emitting diodes [3] and field effect transistors [4]. The development of semiconductor nanomaterials has opened a multitude of applications [5]. CdSe as an important member of semiconductor has direct bulk band gap (1.74 eV), high absorption coefficient and mobility which makes it suitable in devices like laser diodes [6] and high-efficiency luminescent devices [7]. CdSe nanomaterials have band gap comparable to the solar

energy spectrum that makes it suitable in next generation solar cells [8]. In addition to these properties, the electrical properties of CdSe can be enhanced by choosing an appropriate dopant which makes it suitable in various optoelectronic devices like photo detectors [9], field effect transistors [10], photoelectrochemical devices [11] and solar cells [12]. Impurity ions such as Cu [13], In [14], Zn [15], Sn [16], Ag [17] and Pb [18] doped into the CdSe lattice modify the electronic and optical band structure and form a new class of materials. Gawali and Bhosale [11] have found that Al-doped CdSe photoanode gives better performance in terms of photovoltaic power output characteristics as compared with CdSe photoanode and can be used in liquid junction solar cells. Although there is extensive research on tailoring the optical, structural and electrical properties of CdSe nanomaterials by size tunability of quantum dots, addition of dopants, changing the alloy composition etc., but still there is lack of data related to the optical and electronic properties of doped CdSe

Available online at <http://link.springer.com/journal/40195>

J. Kaur · S. K. Tripathi (✉)
Department of Physics, Panjab University, Chandigarh 160014,
India
e-mail: surya@pu.ac.in

nanomaterials after surface treatments, especially in the form of thin films. Nanomaterials deposited in the form of thin films show promising applications in electronic and optoelectronic applications [19]. The properties of thin films depend strongly on the deposition parameters [20], composition of alloy [21], nature of dopant [22], dopant concentration [23] and various heat treatments like thermal annealing [24], post-deposition annealing [25], annealing in nitrogen atmosphere [26], light soaking [27]. Farva and Park [28]. have investigated the effect of annealing in air and nitrogen atmosphere on the morphology and optoelectronic properties of CdSe nanocrystals synthesized by hot injection method and found change in phase from zinc blende to hexagonal upon annealing at 350 °C. They have also synthesized CdSe nanorods by air annealing having improved optoelectronic properties, for solar cell applications [29]. In recent years, focus has been devoted toward the tuning of optoelectronic properties by suitable surface treatments like annealing [30] and surface capping [31]. The electrical and optical properties of thin films play an important role in the device designs. Therefore, it is crucial to find a suitable methodology that can improve the quality and other optoelectronic properties of the thin films. Thermal annealing has been employed to reduce the interparticle separation and modify the electrical conductivity [32]. Post-deposition annealing has also been used by many researchers to enhance the electrical [33] and optical parameters [34].

To the best of our knowledge, there are very few reports available on the study of Ag-doped CdSe thin films. The effect of Ag doping on electrical and optical properties of CdSe has been studied by Sahu et al. [17]. and found that Ag changes from an interstitial (n-type dopant) to substitutional (p-type dopant) with increasing doping level. However, the study of optical and electrical parameters of Ag-doped CdSe nanomaterials after surface treatments has not been comprehensively studied yet. Therefore, in the present paper, we focus on the effect of surface treatments like thermally and optically effects on the optical and electrical properties of Ag-doped CdSe thin films prepared by thermal evaporation technique using inert gas condensation (IGC) method. The as-deposited thin films are annealed and light soaked to study the thermally and optical-induced effects, respectively.

2 Experimental

Bulk material of Ag-doped CdSe was prepared by melt quenching technique as described elsewhere [12]. Constituent elements of Cd (35 at.%), Se (65 at.%) and Ag (1 at.%) were weighed according to their atomic weight percentages and sealed in quartz ampoule under vacuum of

2×10^{-3} Pa. The sealed ampoule was kept inside the furnace for 24 h, which was increased to 1,000 °C at constant heating rate of 2–3 °C/min. During heating process, the ampoule was constantly rocked to obtain homogenous mixture of the alloy. After heating for 24 h, the obtained melt was rapidly quenched in ice cooled water. Thin films of the prepared alloy were made by thermal evaporation [vacuum coating unit HINDHIVAC, Model:VS-65D] using IGC method in the presence of argon as inert gas at room temperature and base pressure of 2×10^{-3} Pa. Well-degassed Corning 7059 glass substrate was used for the substrate of the thin films. The films were kept in deposition chamber in dark before taking any measurements to attain thermodynamic equilibrium.

The microstructure of the thin film was studied by using a Jeol (JSM-6610 LV) scanning electron microscope (SEM) attached with energy dispersive X-ray analyzer (EDX). The composition of the thin film was confirmed by EDX analysis. The prepared thin films were coated with a thin layer of gold (Au) using a SEM sputter coating unit before making SEM and EDX analysis. Transmission electron microscopy (TEM) was done using Hitachi H7500 electron microscope, operating at 100 kV. Film for TEM analysis was prepared on carbon-coated copper grid by thermal evaporation using IGC method. To study the thermally induced effect, as-deposited thin film was annealed for 1 h at 90 °C in a metallic sample holder under vacuum of 2×10^{-1} Pa. To study the optical-induced effect, light from halogen lamp having intensity 7600 lux was shone on the as-deposited thin films through transparent window in a specially designed sample holder under vacuum of 2×10^{-1} Pa for 2 h. Heat radiation during light soaking was eliminated by introducing a water cell in the path of light beam. Light was made to fall on the sample by first passing through a water cell, then light coming from the water cell is made to fall on the thin film placed in the sample holder through a transparent window. The optical transmission data for the as-deposited, annealed and light-soaked thin films were carried out using an UV/VIS/NIR computer-controlled spectrophotometer (Perkin Elmer LAMDA 750) at room temperature. Absorption coefficient was calculated from transmittance and thickness of the films. The thickness of the films was measured using ellipsometric spectroscopy. To study the electrical properties, indium electrodes with a separation of 0.8 mm were made on the as-deposited, annealed and light-soaked thin films using thermal evaporation technique. The dark conductivity is measured using planar geometry of indium electrodes. The voltage across the electrodes is applied using Keithley electrometer (6517A), and current is noted using picoammeter. The conductivity of the film is calculated using relation:

$$\sigma = \frac{L}{A} \frac{I}{V}, \quad (1)$$

where L is the width between the electrodes, A (length of electrode $\times$ thickness of film) is the cross-sectional area, V is the applied voltage and I is the current.

3 Results and Discussion

SEM is used to study the surface morphology of the prepared thin film. Figure 1 shows SEM image of as prepared Ag-doped CdSe thin film. It reveals that the grains are spherical in shape and uniformly distributed all over the surface of the substrate. EDX analysis is carried out to study the composition of the thin film. The composition data of the prepared thin film are given in Table 1, which confirms doping of Ag in CdSe. TEM image of as-deposited thin film is given in Fig. 2. It reveals spherical nature of the nanoparticles having size in the range of 25–30 nm. After surface treatment, the grid generates nanoparticles due to surface diffusion of the metal atoms on the carbon film, which is used to do TEM observation [35]. Therefore, only as-prepared TEM grid has been used for study of shape and size of the nanoparticles.

XRD patterns of as-deposited, annealed and light-soaked Ag-doped CdSe thin films are presented in Fig. 3. XRD patterns consist of an intense peak due to (1 0 0) diffraction plane and two small intensity peaks due to (0 0 2) and (1 1 0) diffraction planes corresponding the hexagonal phase of CdSe (JCPDS 8-459). After annealing treatment, (1 0 0) diffraction peak become sharp, indicating improvement in the crystallinity of the films, which can be attributed to the annealing out of the structural defects as thermal treatment helps the atoms to rearrange themselves and the decrease in defect density. Annealing treatment also helps in thermal expansion of the crystal lattice resulting in the increase in grain size. After light soaking treatment, the sharpness of the peak decreases and peak

Table 1 Elemental analysis of Ag-doped CdSe thin film

Element	wt%	at. %
Se	45.87	62.92
Ag	2.25	1.60
Cd	51.87	35.48

become somewhat broad, which indicate that optical-induced effect degrade the crystal quality. XRD pattern also confirms the phase singularity of the thin films, i.e., the presence of single hexagonal phase and no peak is observed due to silver doping which indicates complete formation of the alloy. The grain size (D) is calculated corresponding the most intense diffraction peak (1 0 0) using the Debye–Scherrer’s formula [16]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (2)$$

where D is the crystallite size, β is the full width at half maximum (FWHM), λ (0.154 nm) is the wavelength of X-rays, and θ is the diffraction angle. The lattice spacing (d) is calculated using Bragg’s diffraction formula $2d \sin \theta = n\lambda$. The lattice strain ε is calculated by using Scherrer’s relation:

$$\varepsilon = \frac{\beta}{4 \tan \theta}. \quad (3)$$

The dislocation density (δ), defined as the length of the dislocation lines per unit volume of the crystal, is evaluated using the formula:

$$\delta = \frac{1}{D^2}. \quad (4)$$

The calculated value of the structural parameters is given in Table 2. Grain size as observed from SEM micrograph seems to be larger than XRD analysis. This

Fig. 1 SEM images of as-deposited Ag-doped CdSe thin film at different magnifications

Fig. 2 TEM images of Ag-doped CdSe thin film at different magnifications

Fig. 3 XRD patterns for as-deposited, annealed and light-soaked thin films

discrepancy between the grain size from XRD and SEM is due to the difference in the principle of techniques as XRD analysis gives grain size of single grains where as SEM micrographs give size of agglomerated grains. Grain size from XRD and from SEM will be almost similar only if the material do not have subgrains, stacking fault or any other planar surface defects. However, it is renowned that during thin film deposition, there are unsaturated bonds, surface defects present due to lattice mismatch between the substrate and the thin film [13]. Therefore, the grain size from XRD and SEM is not similar. The grain size is found to increase after annealing as annealing treatment leads to thermal expansion of the crystal lattice. The increase in the grain size after annealing treatment on CdSe thin films prepared by chemical bath deposition [36] and thermal

evaporation [25] has also been reported earlier. The decrease in grain size after light soaking is ascribed to the increase in surface defect states and disorderness in the material, which causes strain in the material resulting in broadening of peak and decrease in the grain size [37]. X-ray diffraction peaks broaden when the crystal lattice becomes imperfect [38]. Lattice strain is a measurement of the distribution of lattice constants arising from crystal imperfections, such as lattice dislocations. The increase in dislocation density after light soaking reveals that optical-induced effects leads to enhancement of the defects and possesses distortion in the lattice. Furthermore, from Fig. 3, it can be found that after annealing and light soaking of as-deposited thin films position of (1 0 0) peak shifts toward higher diffraction angles indicating the decrease in the lattice parameters.

The transmission spectra of as-deposited, annealed and light-soaked thin films are given in Fig. 4. The absorption edge shifts toward longer wavelength with corresponding decrease in transmittance after annealing and light soaking of as-deposited thin films. The shift in the absorption edge upon surface treatment is much more likely due to the change in structural properties of the film. This decrease in transmittance is attributed to the increase in scattering of photons at the film surface after surface treatments. Shah et al. [39], have also observed the decrease in transmittance after annealing in Ag-doped CdTe thin films prepared by closed-space sublimation technique. The absorption coefficient of the films has been calculated from transmittance using the Lambert's formula [13]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T}, \quad (5)$$

Table 2 Structural parameters of as-deposited, annealed and light-soaked Ag-doped CdSe thin films

Film state	d (10^{-1} nm)	D (nm)	$\delta \times 10^{15}$ (lines/m ²)	ε
As deposited	3.798	19.8	2.55	8.63×10^{-3}
Annealed	3.777	29.9	1.12	5.67×10^{-3}
Light soaked	3.786	16.7	3.58	10.1×10^{-3}

Fig. 4 Transmittance spectra of Ag-doped CdSe thin films; inset shows the variation of absorption coefficient (α) with photon energy ($h\nu$) for as-deposited, annealed and light-soaked Ag-doped CdSe thin films **Fig. 5** Plots of $(\alpha h\nu)^2$ with photon energy, $h\nu$ for as-deposited, annealed and light-soaked Ag-doped CdSe thin films

where d (~ 165 nm is the thickness of the films) and T is the transmittance. The large absorption coefficient of annealed and light-soaked Ag-doped CdSe thin films can find applications in photovoltaic devices. The energy band gap of the thin films is determined from Tauc's relation [13]:

$$(\alpha h\nu) = A(h\nu - E_g)^p, \quad (6)$$

where A is a constant, $h\nu$ is the incident photon energy, E_g is the optical band gap energy, and p is an exponent that

depends on the type of transition involved; e.g., $p = 1/2$ or $3/2$ for allowed direct and forbidden direct interband transitions, respectively, and $p = 2, 3$ for allowed indirect and forbidden indirect interband transitions, respectively. Figure 5 shows the variation of $(\alpha h\nu)^2$ with photon energy, $h\nu$ for the as deposited and after annealing and light soaking of thin films. The extrapolation of the linear part of the curves to the photon energy axis gives the direct optical band gap energy, E_g . The calculated value of E_g for as-deposited, annealed and light-soaked thin films is given in Table 3. Thin films contain a large number of unsaturated bonds or defects that are responsible for the production of localized states in the band gap. There is also formation of surface dangling bonds around the crystallites during the process of crystallization. The value of E_g decreases after annealing and light soaking treatment that is attributed to increase in the width of localized states resulting in narrowing of band gap. The decrease in band gap after annealing is also attributed to the thermal expansion of the crystal lattice that is related to the change in electron energies. Qasrawi [40], have also observed the decrease in band gap after annealing due to temperature dependence of electron phonon interactions and thermal expansion of the lattice.

During surface treatments, bond breaking and bond rearrangements take place, which introduce a change in local structure of the thin films. These include subtle effects such as shift in the absorption edge, more substantial atomic and molecular reconfiguration that is associated with the change in optical constants. The value of refractive index n has been calculated using Manifcer approach which assumes that the sample is a thin film deposited on the transparent substrate [41]. The refractive index in the region, where $\alpha = 0$ is calculated by using equation [41]:

$$n = \sqrt{N + \sqrt{N^2 - s^2}}, \quad (7)$$

$$N = \frac{4s^2}{(s^2 + 1)T^2} - \frac{s^2 + 1}{2}, \quad (8)$$

where s (~ 1.51) is the refractive index of the glass substrate. The refractive index dispersion is shown in Fig. 6a. The decrease in refractive index with wavelength indicates normal dispersion behavior of the investigated thin films. Moreover, the refractive index increases after annealing and light soaking which is attributed to the increase in

Table 3 Optical parameters of as-deposited, annealed and light-soaked Ag-doped CdSe thin films

Film state	E_g (eV)	E_o (eV)	E_d (eV)	n_o	$S_o \times 10^9$ (cm ⁻²)	$\lambda_o \times 10^{-5}$ (cm)	ϵ_o
As deposited	2.16	3.35	9.55	1.96	2.08	3.70	3.84
Annealed	1.94	2.21	8.10	2.16	1.21	5.53	4.66
Light soaked	1.85	2.03	6.13	2.00	0.81	6.11	4.00

Fig. 6 **a** Variation of refractive index, n with wavelength, λ , **b** the optical dispersion behavior, $(n^2 - 1)^{-1}$ versus E^2 for as-deposited, annealed and light-soaked Ag-doped CdSe thin films

absorption coefficient of the film after these surface treatments. Baban et al. [42], have also observed the increase in refractive index after heat treatment on CdSe thin films.

The dispersion of refractive index is further analyzed in the interband region using the single oscillator model and can be expressed by Wemple–DiDomenico (WDD) relation [43]:

$$n^2(E) = 1 + \frac{E_o E_d}{E_o^2 - (E)^2}, \quad (9)$$

where E is the photon energy, E_o is the oscillator energy, and E_d is the dispersion energy which is measurement of strength of the interband optical transitions. This model describes the dielectric response for transitions below the optical band gap. Thus, it plays an important role in determining the behavior of the refractive index. The dispersion parameters E_d and E_o can be obtained according to Eq. (5) by plotting of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ in the interband region as shown in Fig. 6b. The value of E_o and E_d are calculated from the slope and intercept of Fig. 6b and given in Table 3. It is found that E_o and E_d decreases after annealing and light soaking of films. This decrease in E_d and E_o is due to the increase in scattering centers by introduction of localized states after annealing and light soaking treatment. The decrease in oscillator energy also confirms the decrease in optical band gap after surface treatments. Similar behavior of decrease in oscillator energy after surface treatment is also reported by Baban et al. [42], and El-Hagary et al. [43].

The static refractive index n_o is calculated by extrapolating the WDD dispersion relation to the value of the incident photon energy (E) approaching zero, gives:

$$n_o^2 = 1 + \frac{E_d}{E_o}. \quad (10)$$

Moreover, the value of zero frequency dielectric constant $\epsilon_o = n_o^2$ has also been evaluated. The values of n_o and ϵ_o increase after annealing and light soaking and given in Table 3. The refractive index is further analyzed to determine the average interband oscillator strength (S_o) and average interband wavelength (λ_o) by using single Sellmeier oscillator at low energies, where n varies as [43]:

$$\frac{n_o^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda} \right)^2. \quad (11)$$

Further rearranging the above equation gives:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - (\lambda_o/\lambda)^2}, \quad (12)$$

where $S_o = (n_o^2 - 1)/\lambda_o^2$. The calculated values of S_o and λ_o are listed in Table 3. The change in parameters after annealing and light soaking shows that these surface treatments are suitable to modify the refractive index and oscillator parameters.

The effects of annealing and light soaking on the optical conductivity are also studied. The optical conductivity (σ_{opt}) is calculated using relation [43]:

Fig. 7 Variation of optical conductivity, σ_{opt} with wavelength, λ for as-deposited, annealed and light-soaked Ag-doped CdSe thin films

$$\sigma_{\text{opt}} = \frac{\alpha n c}{4\pi}, \quad (13)$$

where α is the absorption coefficient, n is the refractive index, and c is the velocity of light. Figure 7 shows the variation of σ_{opt} as a function of wavelength for the investigated films. The value of σ_{opt} increases after annealing and light soaking of films, which is related to the increase in density of localized states after surface treatments.

The temperature dependence of dark conductivity (σ_d) of as-deposited, annealed and light-soaked Ag-doped CdSe thin films is given in Fig. 8. The conductivity of the films is found to increase with increase in temperature indicating the semiconducting nature of the thin films. There exist two linear regions in Fig. 8a for as-deposited, annealed and light-soaked thin films indicating the presence of two type of conduction band mechanism. The activation energy has been calculated using the Arrhenius equation:

$$\sigma_d = \sigma_{01} \exp\left(\frac{-\Delta E_{d1}}{k_B T}\right) + \sigma_{02} \exp\left(\frac{-\Delta E_{d2}}{k_B T}\right), \quad (14)$$

where σ_{01} and σ_{02} are the material-dependent parameters, ΔE_{d1} and ΔE_{d2} are the dark activation energies, k_B is the Boltzmann's constant, and T is the absolute temperature. The first term dominating in the high temperature range corresponds to the conduction band mechanism, and second term corresponds to the hopping conduction of charge carriers through the localized states. The value of σ_d at room temperature and activation energies in the high temperature region (HTR) and low temperature region (LTR) is given in Table 4. It is found that value of σ_d increases after annealing treatment that is ascribed to the increase in grain size eventually decrease in the grain boundary potential of the charge carriers, thus enhancing the mobility and increasing the conductivity of the film. Kale and Lokhande [44], have also observed the increase in conductivity of chemically deposited nanocrystalline CdSe thin films after annealing treatment due to the increase in grain size. The decrease in σ_d after light soaking treatment is attributed to the decrease in grain size due to imperfections in the crystal lattice resulting in increase in grain boundary potential which in turn decrease the conductivity. After light soaking, there is also increase in dislocation centers and defect states, the charge carriers can be trapped in these defect states and become immobile resulting in decrease in conductivity of charge carriers. Thus, reduced conductivity is attributed to the enhanced recombination of carriers via trapping at defect centers produced by optical-induced effect. At low temperature, hopping conduction in the localized states near the Fermi level is dominant. The hopping conduction is associated with the electron jumping from the occupied donor states to empty ones. The variable range hopping at low temperature is characterized by Mott's relation [16]:

$$\sigma T^{1/2} = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right], \quad (15)$$

Fig. 8 a Variation of $\ln \sigma_d$ versus $1,000/T$, b Plots of $\ln \sigma T^{1/2}$ versus $T^{-1/4}$ for as-deposited, annealed and light-soaked thin films

Table 4 Electrical parameters of as-deposited, annealed and light-soaked Ag-doped CdSe thin films

Film state	σ_d ($\Omega^{-1} \text{ cm}^{-1}$)	ΔE_a (eV)		T_o (K)	$N(E_F)$ ($\text{cm}^{-3} \text{ eV}^{-1}$)	R (cm)	W (eV)	$\alpha'R$
		HTR	LTR					
As deposited	2.24×10^{-8}	0.634	0.039	5.32×10^6	7.49×10^{19}	4.23×10^{-7}	0.042	5.24
Annealed	1.43×10^{-7}	0.497	0.031	2.61×10^6	1.52×10^{20}	3.54×10^{-7}	0.035	4.39
Light soaked	1.45×10^{-9}	0.36	0.028	1.71×10^6	2.33×10^{20}	3.18×10^{-7}	0.032	3.94

where σ_o is the pre-exponential factor, and T_o is inversely related to the density of localized states near the Fermi level by the relation:

$$T_o = C_o \frac{\alpha'^3}{kN(E_F)}, \quad (16)$$

where C_o (≈ 18) is the dimensionless constant, α' is the decay constant of the wave function of the localized states near the Fermi level and is assumed to be 1.24 nm^{-1} . The experimental data obey Mott's relation, giving rise to a linear relationship between $\ln(\sigma T^{1/2})$ and $(T^{-1/4})$ as is clear from Fig. 8b. Therefore, the conduction mechanism at low temperature is due to the hopping of the charge carriers among the localized states. Hopping distance (R) and hopping energy (W) are also calculated from the density of states using the following relations:

$$R = \left[\frac{9}{8\pi\alpha'kTN(E_F)} \right]^{1/4}, \quad (17)$$

$$W = \frac{3}{4\pi R^3 N(E_F)}. \quad (18)$$

The calculated values of T_o , R , $N(E_F)$ and W are given in Table 4. The value of T_o near the Fermi level decreases after annealing and light soaking of thin films, resulting in the increase in density of localized states near the Fermi level, $N(E_F)$. The increase in density of localized states attributes to charge carriers require less energy and distance to hop from one localized state to another one and therefore decrease in hopping distance and hopping energy. It is also found from Table 4 that values of $\alpha'R$ and W are greater than unity and kT , respectively, which agrees well with the Mott's condition of hopping conduction. Degree of localization of the carriers in the trap states, indicated by $\alpha'R > 1$, shows that the charge carriers are highly localized.

To measure the carrier concentration and type of majority charge carriers, the Hall effect has been studied on the thin films. From the results of Hall measurements, we have observed negative sign of Hall voltage for as-deposited, annealed and light-soaked thin films which indicates n-type behavior of the films. The values of carrier mobility (μ_H) and carrier concentration (n) for as-deposited, annealed and light-soaked thin films are given in

Table 5 Carrier concentration (n) and mobility (μ_H) of the charge carriers for as-deposited, annealed and light-soaked Ag-doped CdSe thin films

Film state	μ_H ($\text{cm}^2/\text{V s}$)	n (cm^{-3})
As deposited	13.12	1.07×10^{10}
Annealed	77.05	1.20×10^{10}
Light soaked	3.43	2.64×10^9

Table 5. It is observed from Table 5 that the carrier concentration (n) and mobility (μ_H) increase after annealing and decrease after light soaking treatment of as-deposited thin films. The increase in mobility of charge carriers after annealing of Ag-doped CdS thin films is also reported by Taur et al. [45].

The mobility of the charge carriers is strongly affected by grain boundary scattering. Annealing treatment anneals out structural defects and increases the grain size as observed from XRD analysis, resulting in the decrease of the grain boundary potential. The decrease in grain boundary potential in turn increases the mobility and concentration of charge carriers, which results in the increase in the conductivity. The light-induced effects disturb the crystal structure and increase the dislocation density as evident from XRD analysis. After light soaking treatment, decrease in grain size results into trapping of charge carriers and increase in grain boundary potential, which results in the decrease in mobility and concentration of charge carriers. This decrease in carrier concentration after light soaking is responsible for observed decrease in conductivity. The decrease in conductivity is due to the enhanced recombination of carriers via trap states induced by light soaking treatment. This implies that after light soaking treatment in addition to the increase in the width of localized states, there is also increase in trapping of charge carriers, which make them immobile and decreases the mobility of charge carriers, consequently decreases the conductivity. The formation of trap states shortens the life time of charge carriers and promotes recombination of carriers, having adverse effect on the semiconductor device performance. However, in case of annealing treatment, both the absorption coefficient and conductivity increases. The increase in conductivity and absorption after annealing of thin films can give better cell performance in the solar cell

and optoelectronic devices as compared to light-soaked Ag-doped CdSe thin films.

4 Conclusions

Thin films of the Ag-doped CdSe are prepared by thermal evaporation technique using inert gas condensation method. The elemental composition of the thin films is analyzed by EDX. SEM study reveals the uniform distribution of the grains over the glass substrate. TEM analysis reveals that the nanoparticles are spherical in shape having average particle size 25–30 nm. XRD analysis reveals that the grain size increases after annealing and decrease after light soaking treatment of as-deposited thin films. From XRD analysis, it is found that thermally induced effects anneal out structural defects and optical-induced effects leads to enhancement of defects in the lattice. The transmission spectra and band gap energy are found to decrease after annealing and light soaking of thin films. The decrease in band gap after annealing and light soaking is attributed to the introduction of localized states in the band gap. Wemple–DiDomenico relation describes the optical parameters in the interband region. The increase in dark conductivity after annealing is attributed to the increase in grain size resulting in decrease in grain boundary potential, whereas decrease in conductivity after light soaking is due to the decrease in grain size with corresponding increase in grain boundary potential and trapping of carriers at trap states. The hopping distance and hopping energy decrease after annealing and light soaking of Ag-doped CdSe thin films. Hall effect measurements revealed n-type behavior of the as-deposited, annealed and light-soaked thin films.

Acknowledgments This work was financially supported by University Grant Commission (UGC) [F.No. 42-781/2013(SR)], New Delhi. Ms. Jagdish Kaur is thankful to UGC, N. Delhi for providing the fellowship.

References

- [1] L. Du, Y. Lei, Mater. Lett. **106**, 100 (2013)
- [2] J. Li, J.Z. Zhang, Coord. Chem. Rev. **253**, 3015 (2009)
- [3] R. Yu, Q. Lin, S.F. Leung, Z. Fan, Nano Energy **1**, 57 (2012)
- [4] J. Jie, W.Z.I. Bello, C.S. Lee, S.T. Lee, Nano Today **5**, 313 (2010)
- [5] H.K.E. Latha, A. Udayakumar, V.S. Prasad, Acta Metall. Sin. (Engl. Lett.) **27**, 168 (2014)
- [6] H.J. Eisler, V.C. Sundar, M.G. Bawend, M. Walsh, H.I. Smith, V. Klimov, Appl. Phys. Lett. **80**, 4614 (2002)
- [7] C. Wang, B.L. Wehrenberg, C.Y. Woo, P.G. Sionnest, J. Phys. Chem. B **108**, 9027 (2004)
- [8] P. Mahawela, S. Jeedigunta, S. Vakkalanka, C.S. Ferekides, D.L. Morel, Thin Solid Films **480**, 466 (2005)
- [9] V. Chikan, J. Phys. Chem. Lett. **2**, 2783 (2011)
- [10] C. Liu, P. Wu, T. Sun, L. Dai, Y. Ye, R. Ma, G. Qin, J. Phys. Chem. C **113**, 14478 (2009)
- [11] S.A. Gawali, C.H. Bhosale, Mater. Chem. Phys. **129**, 751 (2011)
- [12] S.K. Shinde, D.P. Dubal, G.S. Ghodake, V.J. Fulari, Mater. Lett. **126**, 17 (2014)
- [13] K. Sharma, A.S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi, J. Alloys Compd. **540**, 198 (2012)
- [14] A.S. Al-Kabbi, K. Sharma, G.S.S. Saini, S.K. Tripathi, J. Alloys Compd. **555**, 1 (2013)
- [15] H.M. Ali, H.A.A. El-Ghanny, J. Phys.: Condens. Matter **20**, 155205 (2008)
- [16] K. Sharma, A.S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi, J. Alloys Compd. **564**, 42 (2013)
- [17] A. Sahu, M.S. Kang, A. Kompch, C. Notthoff, A.W. Wills, D. Deng, M. Winterer, C.D. Frisbie, D.J. Norris, Nano Lett. **12**, 2587 (2012)
- [18] J. Kaur, S.K. Tripathi, J. Alloys Compd. **622**, 953 (2015)
- [19] L. Korala, Z. Wang, Y. Liu, S. Maldonado, S.L. Brock, ACS Nano **7**, 1215 (2013)
- [20] S.S. Kale, C.D. Lokhande, Mater. Chem. Phys. **62**, 103 (2000)
- [21] S.N. Sarangi, S.N. Sahu, Physica E **23**, 159 (2004)
- [22] S.K. Tripathi, A.S. Al-Kabbi, K. Sharma, G.S.S. Saini, Thin Solid Films **548**, 406 (2013)
- [23] A.B. Yadav, A. Pandey, S. Jit, Acta Metall. Sin. (Engl. Lett.) **27**, 682 (2014)
- [24] M. Arslan, R. Muhammad, A. Mahmood, R. Rasheed, Acta Metall. Sin. (Engl. Lett.) **26**, 699 (2013)
- [25] E. Bacaksiz, B.M. Basol, M. Altunbas, S. Yilmaz, M. Tomakin, B. Abay, Phys. Status Solidi B **244**, 497 (2007)
- [26] S. Erat, H. Metina, M. Ari, Mater. Chem. Phys. **111**, 114 (2008)
- [27] K. Sharma, A.S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi, Curr. Appl. Phys. **13**, 964 (2013)
- [28] U. Farva, C. Park, Sol. Energy Mater. Sol. Cell **94**, 303 (2010)
- [29] U. Farva, C. Park, Mater. Lett. **64**, 1415 (2010)
- [30] S.K. Min, O.S. Joo, R.S. Mane, K.D. Jung, C.D. Lokhande, S.H. Han, J. Photochem. Photobiol. A **187**, 133 (2007)
- [31] H.J. Choi, J.K. Yang, H.H. Park, Thin Solid Films **494**, 207 (2006)
- [32] P.P. Hankare, P.A. Chate, D.J. Sathe, A.A. Patil, J. Mater. Sci.: Mater. Electron. **20**, 776 (2009)
- [33] S. Levichev, A. Chahboun, A.G. Rolo, O. Conde, M.J.M. Gomes, Thin Solid Films **517**, 2538 (2009)
- [34] C. Shao, X. Meng, P. Jing, M. Sun, J. Zhao, H. Li, J. Lumin. **142**, 196 (2013)
- [35] Z. Zhang, D.-S. Su, Ultramicroscopy **109**, 766 (2009)
- [36] T.S. Shyju, S. Anandhi, R. Indirajith, R. Gopalakrishnan, J. Alloys Compd. **506**, 892 (2010)
- [37] K. Venkateswarlu, A. ChandraBose, N. Rameshbabu, Phys. B **405**, 4256 (2010)
- [38] T. Ungar, Scr. Mater. **51**, 777 (2004)
- [39] N.A. Shah, A. Ali, A.K.S. Aqili, A. Maqsood, J. Cryst. Growth **290**, 452 (2006)
- [40] A.F. Qasrawi, Semicond. Sci. Technol. **20**, 765 (2005)
- [41] K. Sharma, A.S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi, Mater. Res. Bull. **47**, 1400 (2012)
- [42] C. Baban, G.I. Rusu, P. Prepelita, J. Optoelectron. Adv. Mater. **7**, 817 (2005)
- [43] M. El-Hagary, M. Emam-Ismael, E.R. Shaaban, A. Al-Rashidi, S. Althoyaib, Mater. Chem. Phys. **132**, 581 (2012)
- [44] R.B. Kale, C.D. Lokhande, Appl. Surf. Sci. **223**, 343 (2004)
- [45] V.S. Taur, R.A. Joshi, R. Sharma, Int. J. Photoenergy **2012**, 264027 (2012)