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Effect of Ag in CdSe thin films prepared using thermal evaporation

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It has been a general practice to dope thin films with suitable dopants to modify the properties of the films to make them more suitable for potential applications. When the dopant concentrations are low, they do not normally affect the structure and morphology of the films. However, it may lead to drastic changes in electronic properties of the films. This might result from the dopant getting incorporated into the lattice of the material of the films. Cadmium selenide is an important compound semiconductor material with an attractive energy band gap. The present work relates to an attempt made to dope CdSe thin films with silver. CdSe : Ag (1 to 5%) thin films were deposited on glass substrates at an optimized substrate temperature of 453 K using thermal evaporation technique. The grown films were analyzed using X-ray diffraction, scanning electron microscopy (SEM), energy dispersive analysis of X-ray (EDX) techniques. It is observed that undoped CdSe thin films and CdSe : Ag films have hexagonal structure. The grain size was found to increase marginally with an increase in the Ag concentration. The optical band gap of the films determined by optical transmission measurements agree with that of CdSe. Electrical conductivity is observed to increase from 10^{-4} to $3.66\,(\Omega \cdot \mathrm{cm})^{-1}$ on addition of silver. The variation of resistance with temperature indicates that the prepared films consist of CdSe and Ag existing as two separate phases coexisting and contributing individually to the resistivity of the films.

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1. Introduction

In II–VI group of compounds, CdSe is one of the extensively studied compound semiconductors. With a band gap of 1.74 eV it is considered as a promising material for device applications such as solar cell window absorber layer, photo detectors, gas sensors, field effect transistors [1]. Properties of thin films depends on growth techniques and preparation conditions. Several preparation techniques are used to prepare CdSe thin films including thermal evaporation [2], chemical bath deposition [3], spray pyrolysis and [4] solution growth method [5].

Number of researchers worked on the doping of cadmium selenide [6–20] and also on photoconductivity, electrical and optical properties of Ag doped CdSe thin films obtained using solution growth, thermal evaporation and ion exchange method [5–15]. CdSe is basically n-type material in bulk as well as in thin film form having a high resistance. CdSe thin films with low resistivity can be used in heterojunction solar cells to lower the series resistance and to minimize the conduction Band-to-Fermi level energy separation [16]. Substrate temperature, deposition rate, vacuum condition, post deposition annealing condition and wafers plays important role in the preparation of thin films. The electrical and optical properties of semiconductors are strongly influenced by doping process [17]. Agglomeration of Ag in doped CdSe thin films has been studied by scanning electron microscopy. It has been reported that silver remains as separate clusters when used for doping CdSe thin films [6]. Tailoring the electrical and optical properties of cadmium selenide by doping makes it suitable in next generation solar cells because of its optical band gap lying the solar energy spectrum.

The evaluation of any material for application is complete and meaningful only when its structure, composition and properties are well known. Thermal evaporation is often used because of its possibilities to vary the deposition parameters to get stoichiometric films. The study of doping effect on the properties of CdSe thin films is still insufficient to know the behavior of material prepared in different conditions. In the present work, preparation of undoped and CdSe : Ag thin films were carried out by thermal evaporation technique. Effect of addition of Ag on structural, morphological, compositional, electrical and optical properties of CdSe thin film samples is studied in detail.

2. Experimental method

Undoped and CdSe : Ag thin films were prepared on glass substrates using thermal evaporation technique at a pressure less than $5 \cdot 10^{-6}$ Torr. Substrates were dipped in chromic acid for 24 h to eradicate the contaminations on the surface of the substrate. These were further cleaned by detergent and rinsed with acetone. Cleaned substrates were heated to and maintained at 453 K for 2 h prior to film deposition. Tantalum boat was used to evaporate cadmium selenide (CdSe) fine powder of purity 99.995% and silver

(Ag) powder of 99.99% (Alfa Aesar). Stoichiometric CdSe thin films were obtained at a substrate temperature of 453 K and this condition was maintained throughout the series of experiments. Deposition rate was maintained at 0.4 nm/sec. Two sets of samples were prepared and were annealed at two different conditions. One set of samples were annealed at 473 K for 2 h in air and other in vacuum.

The thickness of the prepared films was determined by gravimetric method and it was found to be in the range of 750 to 800 nm. Structural characterization has been carried out using X-ray diffraction (Rigaku Miniflex 600 with CuK_α radiation of wavelength 1.5406 Å in the 2θ range from 20 to 60°. Scanning electron microscope (Carl Zeiss) has been used to record the surface micrographs of undoped and CdSe : Ag thin films. Elemental analysis has been carried out using Energy Dispersive X-ray (EDX) attached to the SEM. Absorption spectra of undoped and CdSe : Ag thin films were recorded using Shimadzu make UV-Vis-NIR 3600 spectrophotometer in the wavelength range of 300−1400 nm. For electrical studies silver contacts were deposited on CdSe and CdSe : Ag thin films in coplanar structure. Resistance has been measured as a function of temperature ranging from 300 to 473 K to evaluate the activation energy for conduction.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD patterns of undoped CdSe thin films. The crystallite size (D) of the undoped and Ag-doped CdSe films was determined using the Scherer's equation:

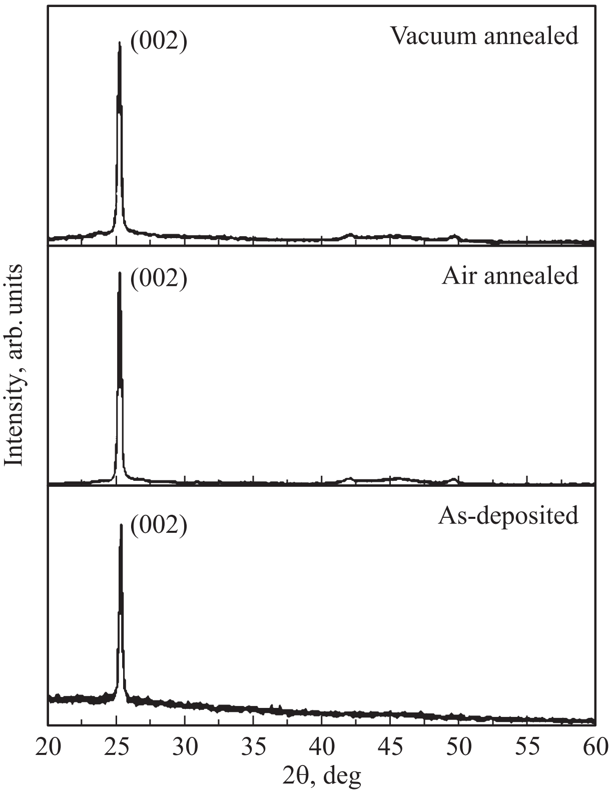

Figure 1. X-ray diffraction patterns of undoped CdSe thin films.

Table 1. XRD data of air annealed undoped and Ag doped CdSe thin films

Sample	2θ, deg	d, Å	Plane	D, nm
As deposited	25.47	3.49	(002)	28.44
As deposited air annealed	25.28	3.52	(002)	35.23
Ag 1%	25.30	3.51	(002)	33.35
Ag 2%	25.33	3.51	(002)	39.69
Ag 3%	25.34	3.51	(002)	40.89
Ag 5%	25.35	3.50	(002)	43.29

Table 2. XRD data of vacuum annealed undoped and Ag doped CdSe thin films

Sample	2θ, deg	d, Å	Plane	D, nm
As deposited	25.47	3.49	(002)	28.44
As deposited vacuum annealed	25.29	3.52	(002)	31.58
Ag 1%	25.30	3.52	(002)	29.58
Ag 2%	25.31	3.51	(002)	32.29
Ag 3%	25.35	3.51	(002)	38.03
Ag 5%	25.44	3.50	(002)	39.52

$$D = \frac{K\lambda}{\beta\cos\theta}, \tag{1}$$

where the Scherer constant K is taken equal to 0.9, D is crystalline size and β is full width at half maximum in radians and θ is the Bragg's angle corresponding to the prominent peak [8].

The diffraction patterns were indexed on a hexagonal lattice and the lattice parameters were evaluated from the following relation:

$$\frac{1}{d^2} = \frac{4}{3}\frac{(h^2 + hk + k^2)}{(a^2)} + \frac{l^2}{c^2}. \tag{2}$$

Variation of crystallite size and lattice parameters, are tabulated in Tables 1 and 2 for air annealed and vacuum annealed films, respectively. A careful observation made on the calculated lattice parameters indicate good agreement with standard data for hexagonal lattice (JCPDs card 08-0459). Fig. 2, a, b show the XRD traces for air annealed and vacuum annealed CdSe : Ag thin films. XRD analysis reveals that the films are polycrystalline in nature processing hexagonal crystal structure.

There is no peak corresponding to free silver or related compound detected in the XRD pattern. No significant change was observed in crystallite size with doping in air annealed as well as for vacuum annealed CdSe : Ag films.

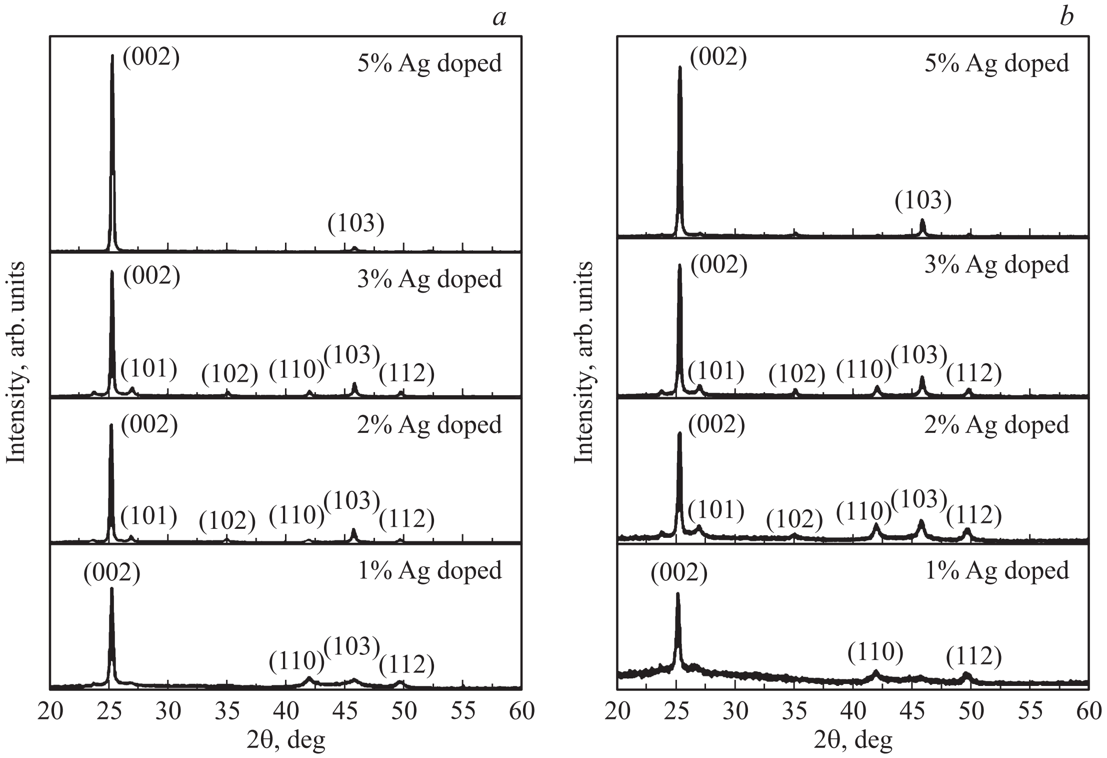

Figure 2. XRD patterns of Ag doped CdSe thin films (*a*) air annealed (*b*) vacuum annealed.

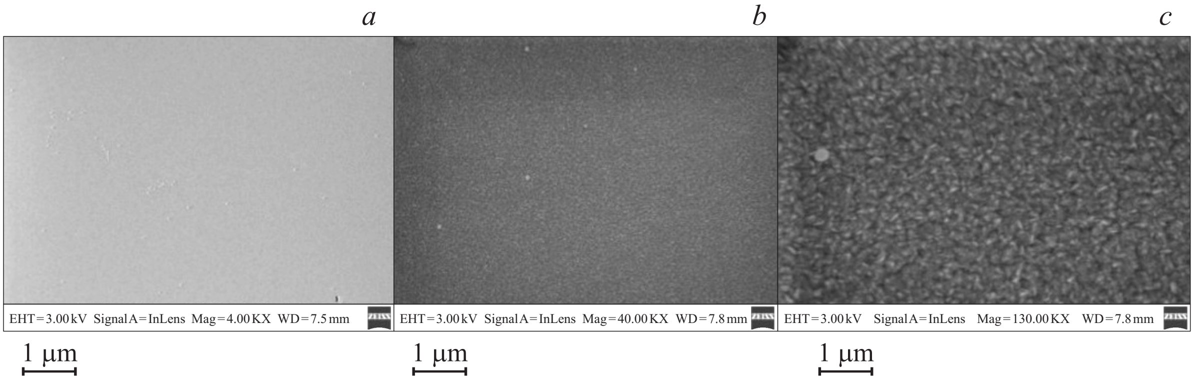

Figure 3. SEM micrographs of (*a*) as-deposited, (*b*) air annealed, (*c*) vacuum annealed undoped CdSe thin films.

An increase in the dopant concentration does not result in any changes in lattice parameter indicating that there is no lattice distortion.

3.2. Surface morphological analysis

The surface morphology of thermally evaporated undoped and CdSe:Ag thin films was investigated using scanning electron microscopy (SEM) technique. Fig. 3 shows SEM micrographs of undoped CdSe thin films. It has been found that the as-deposited CdSe thin films were uniform and featureless. It was also observed that crystallite size increases marginally on annealing the nanocrystalline CdSe thin films in both air and vacuum. Fig. 4, 5 show SEM micrographs of air annealed and vacuum annealed CdSe:Ag thin films, respectively. It is observed that the surface roughness increases with increasing Ag concentration.

The EDX analysis of the undoped films revealed the dependence of the film composition on the annealing condition. This was expected in thermally evaporated compound materials. The vapor pressure and sticking coefficient of cadmium and selenium are different, when CdSe powder is thermally evaporated, it dissociates into cadmium and selenium. Since cadmium and selenium have different vapor pressure, varying amount of cadmium and selenium reach the substrate where they recombine to form CdSe. To get stoichiometric CdSe films substrate temperature was varied from 300 to 523 K. The post deposition annealing of the

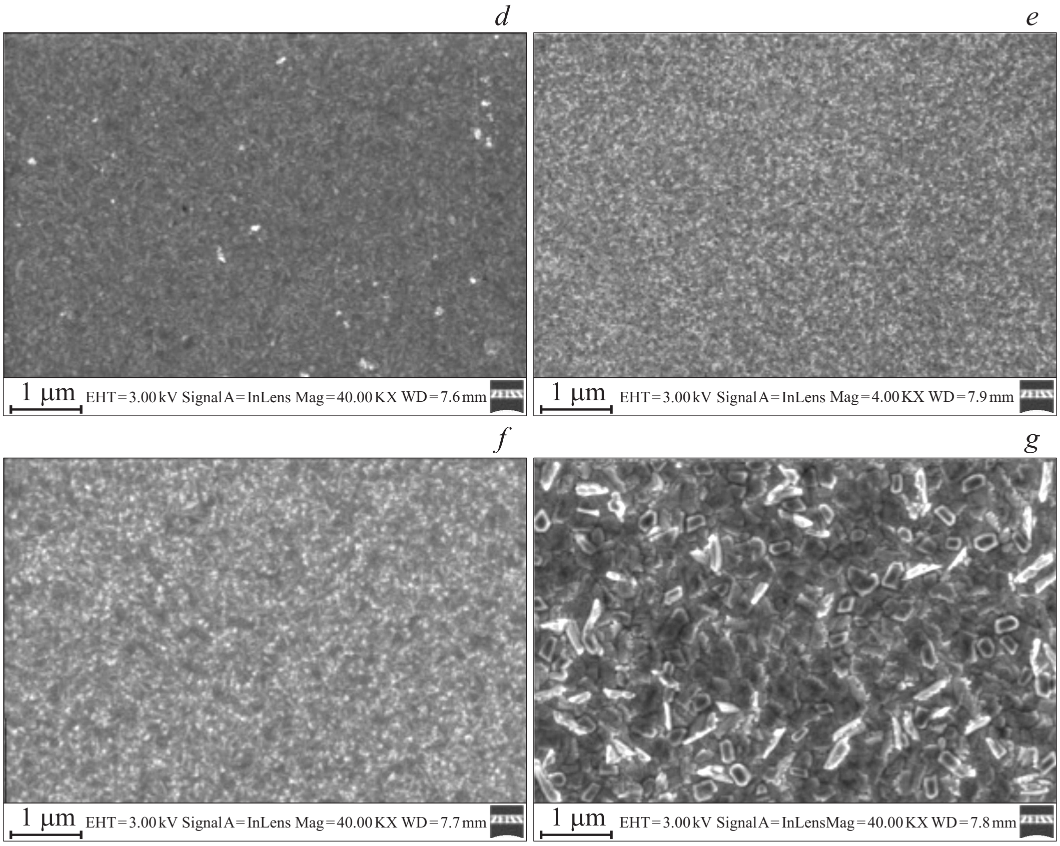

Figure 4. SEM micrographs of air annealed CdSe:Ag thin films. Dopant concentrations are (*d*) 1, (*e*) 2, (*f*) 3, and (*g*) 5%.

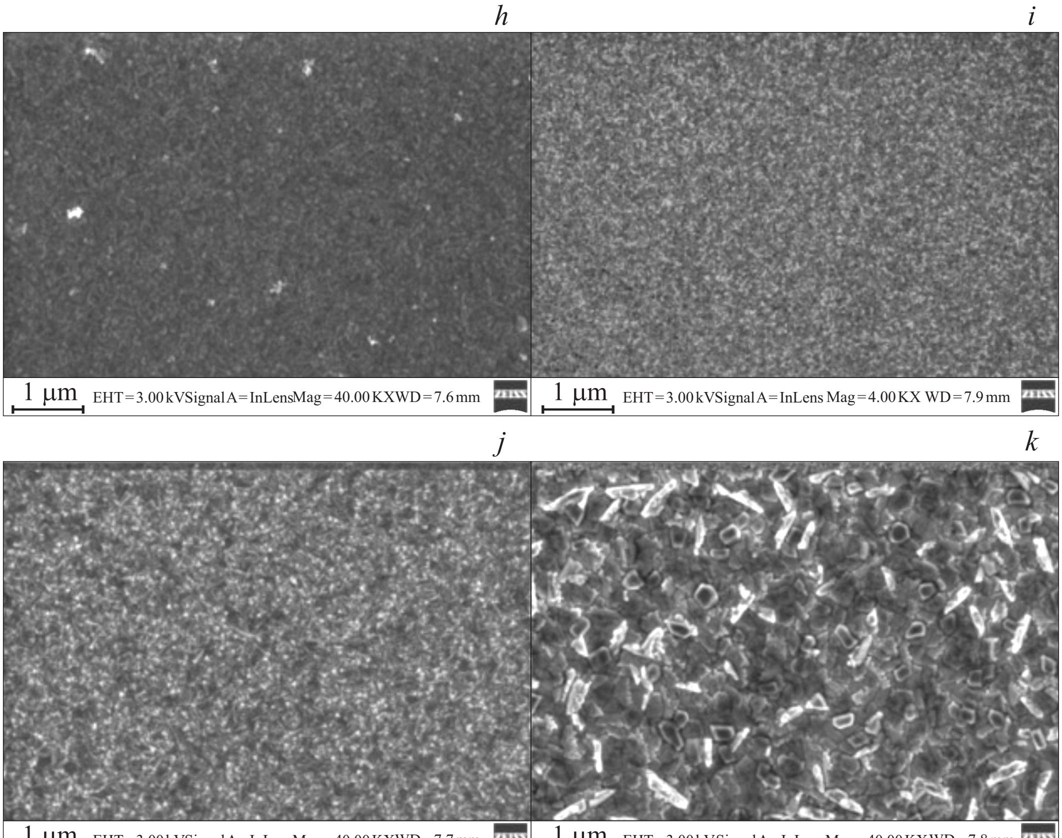

Figure 5. SEM micrographs of vacuum annealed CdSe:Ag thin films. Dopant concentrations are (*h*) 1, (*i*) 2, (*j*) 3, and (*k*) 5%.

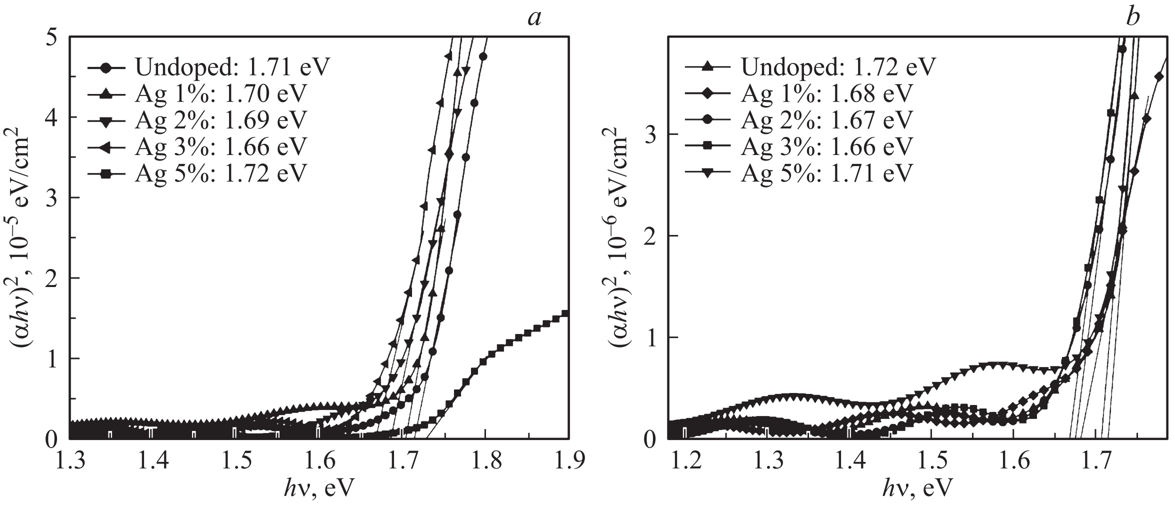

Figure 6. Tauc's plot of undoped and CdSe : Ag thin films. (*a*) air annealed and (*b*) vacuum annealed.

films in vacuum also changed the film composition due to re-evaporation of excess selenium. The conductivity of the films depends on the composition of Cd : Se ratio. In the present work, stoichiometric composition was achieved at a substrate temperature of about 453 K. Those deposited at suboptimum conditions were deficient or excess in any one of the elements. This substrate temperature was optimized to prepare undoped and CdSe : Ag films.

3.3. Optical properties

Fig. 6, *a*, *b* show the plots of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ for air annealed and vacuum annealed samples respectively. Optical band gap (E_g) values were determined by standard Tauc's method [3]. The optical band gap (E_g) values were deduced by extrapolating the linear portion of the respective curves to $(\alpha h\nu)^2 = 0$.

The relation between the optical band gap (E_g) and absorption coefficient (α) is given by

$$(\alpha h\nu)^2 = B(h\nu - E_g)^n \tag{3}$$

where $h\nu$ is the photon energy, B is a proportionality constant and the exponent n depends on the type of optical transition. A suitable value of n is used to linearize the graph. The best fit is found to be for $n = 1/2$ which indicates the direct allowed transition [9]. The optical band gap values are listed in the Table 3, for air annealed and vacuum annealed samples. No significant change in the optical band gap was observed for air annealed and vacuum annealed CdSe : Ag films with increasing Ag concentration.

Table 3. Optical band gap of undoped and CdSe : Ag thin films

Ag (Wt.%)	Air annealed	Vacuum annealed
	E_g (eV)	
0	1.71	1.72
1	1.70	1.68
2	1.69	1.67
3	1.66	1.66
5	1.72	1.71

3.4. Electrical properties

Electrical resistivity and temperature dependence of resistance measurements have been carried out for undoped and CdSe : Ag (1 to 5%) thin films in the temperature range from 300 to 473 K. The resistance of films decreased with increased temperature indicating the semiconducting nature. The hot probe method reveals that as deposited, annealed and CdSe: Ag thin films have *n*-type conduction. Activation energy was calculated from the slope of the linear portion obtained from the plot of $\ln R vs 10^3/T$ (Fig. 7).

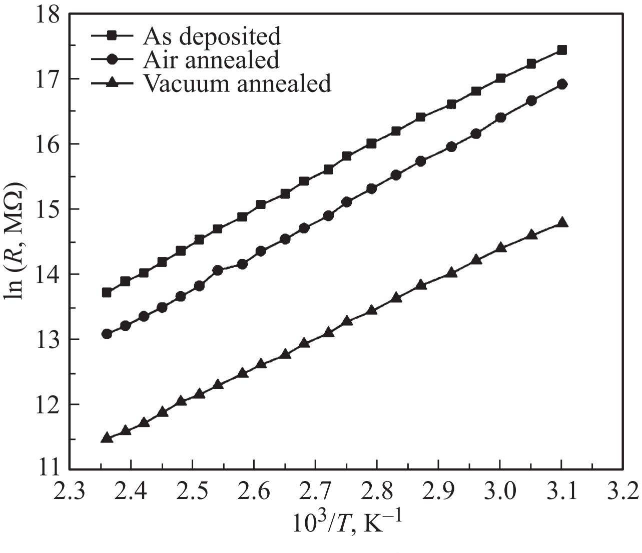

Figure 7. Plot of $\ln(R) vs 1000/T, \mathrm{K}^{-1}$ for undoped CdSe thin films.

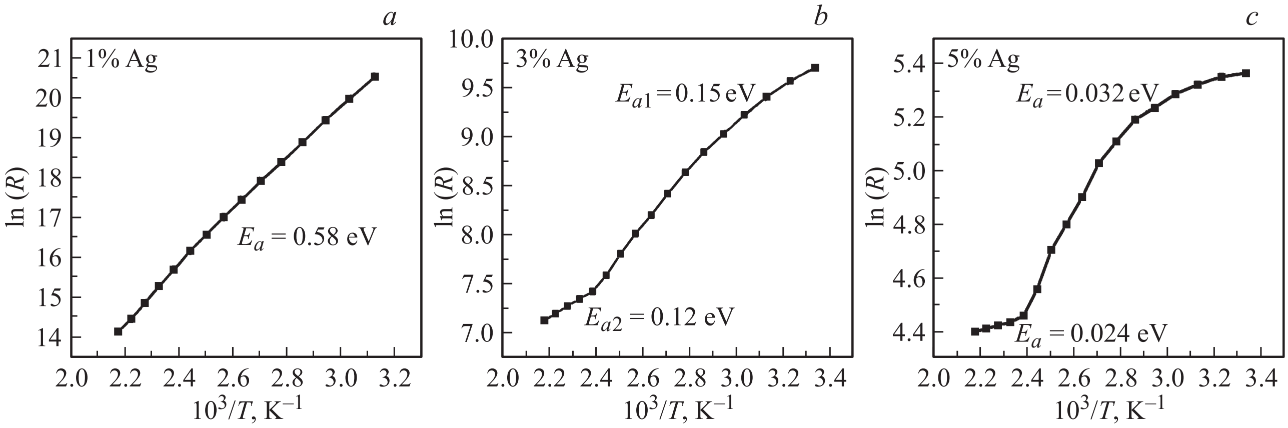

Figure 8. Plot of $\ln(R) vs 1000/T, \mathrm{K}^{-1}$ for CdSe : Ag thin films with (*a*) 1, (*b*) 3, and (*c*) 5% Ag.

The plot obeys the relation,

$$\sigma = \sigma \cdot \exp\left(-\frac{E_a}{kT}\right) \tag{4}$$

where E_a — is the activation energy, k — the Boltzmann constant and T — the temperature in Kelvin.

Activation energy was found to be 0.45, 0.44 and 0.39 eV for as deposited, air annealed and vacuum annealed CdSe films respectively. The calculated electrical conductivity is listed in the Table 4 for air annealed and vacuum annealed films. Room temperature conductivity of undoped CdSe thin films was found to be of the order of 10^{-4} $(\Omega \cdot \mathrm{cm})^{-1}$. In case of air annealed undoped CdSe films, the conductivity decreases as compared to that of as-deposited films, due to oxygen incorporation into CdSe thin films. The incorporated oxygen acts as an acceptor impurity in annealed films [12]. In case of vacuum annealed undoped CdSe films, conductivity increases which may be due to re-evaporation of Se content from the deposited film while annealing as confirmed by EDX analysis. The composition analysis using EDX also reveals that addition of silver to the films result in a decrease in the concentration of both cadmium and selenium. This indicates that silver does not replace either cadmium or selenium preferentially.

A detailed study of variation of resistance with temperature for the case of CdSe : Ag films shows that the electrical resistivity decreases with increase in the silver content in the films (Fig. 8). Further, the activation energy for conduction is observed to decrease at higher temperature ranges which cannot be explained by the normal semiconducting nature of the films. If the films show a transition from extrinsic conduction to intrinsic conduction, the activation energy should be higher at higher temperature range. These observations point towards the possibility of silver remaining as a metallic phase along with CdSe in the films. This is further confirmed by the fact that the X-ray studies did not show any variation in the crystal structure data and the minute amount of silver does not show up in the X-ray diffraction pattern. The X-ray peak analysis also point to the fact that the grain size and micro strain in the films are unaltered on addition of silver. The scanning electron micrographs show the films to have a rough surface with probable precipitates of silver. It is concluded that silver does not dope CdSe thin films and does not replace any of the components in the film but remain as a passive additive in the films.

Table 4. Electrical conductivity data for undoped and CdSe : Ag thin films

Ag (Wt.%)	Air annealed	Vacuum annealed
	σ, $(\Omega \cdot \mathrm{cm})^{-1}$	
0	$0.48 \cdot 10^{-4}$	$3.87 \cdot 10^{-4}$
1	$1.2 \cdot 10^{-3}$	$3.29 \cdot 10^{-6}$
2	$0.21 \cdot 10^{-2}$	$1.45 \cdot 10^{-2}$
3	$3.64 \cdot 10^{-1}$	$4.2 \cdot 10^{-1}$
5	3.66	1.04

4. Conclusions

The stoichiometric CdSe thin film was obtained at 453 K substrate temperature by high vacuum thermal evaporation. Undoped and CdSe : Ag thin films show polycrystalline hexagonal structure. There is no significant change in lattice parameters as well as the optical band gap of air annealed and vacuum annealed CdSe films with increasing Ag concentration. It is concluded that silver does not get incorporated into the lattice of CdSe. However, the increase in electrical conductivity is explained as due to the presence of Ag as a separate metal phase.

References

[1] A.S. Al-Kabbi, K. Sharma, G.S.S. Saini, S.K. Tripathi. J. Alloys Comp., **555**, 1 (2013).

[2] C. Baban, G.I. Rusu. Appl. Surf. Sci., **211**, 6 (2003).

[3] R.S. Mane, C.D. Lokhande. Mater. Chem. Phys., **65** (1), 1 (2000).
[4] A.A. Yadav, M.A. Barote, E.U. Masumdar. Mater. Chem. Phys., **121** (1–2), 53 (2010).
[5] K.S. Sharma, R. Sharma, J.C. Garg. Jpn. J. Appl. Phys., **31**, 742 (1992).
[6] J. Kaur, S.K. Tripathi. Acta Metall. Sin. Engl. Lett., **28** (5), 591 (2015).
[7] T. Elango, V. Subramanian, K.R. Murali. Surf. Coat. Technol., **123** (1), 8 (2000).
[8] K. Sharma, A.S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi. J. Alloys Comp. **564**, 42 (2013).
[9] K. Sharma, A.S. Al-Kabbi, G.S.S. Saini, S.K. Tripathi. J. Alloys Comp. **540**, 198 (2012).
[10] E.U. Masumdar, V.B. Gaikwad, V.B. Pujari, P.D. More, L.P. Deshmukh. Mater. Chem. Phys., **77** (3), 669 (2003).
[11] K.C. Sathyalatha, S. Uthanna, P.J. Reddy. Thin Sol. Films, **174**, pt 1, 233 (1989).
[12] H. Mahfoz Kotb, M.A. Dabban, F.M. Abdel-Rahim, A.Y. Abdel-latif, M.M. Hafiz. **406** (6–7), 1326 (2011).
[13] K.N. Shreekanthan, B.V. Rajendra, V.B. Kasturi, G.K. Shivakumar. Cryst. Res. Technol., **38** (1), 30 (2003).
[14] A. Sahu, M.S. Kang, A. Kompch, C. Notthoff, A.W. Wills, D. Deng, D. Norris. J. Nano Lett., **12** (5), 2587 (2012).
[15] S.S. Kale, C.D. Lokhande. Mater. Chem. Phys., **62** (2), 103 (2000).
[16] S. Chander, M.S. Dhaka. Phys. E: Low-Dim. Systems and Nanostructures, **76**, 52 (2016).
[17] A. Ali, N. Abbas Shah, A. Maqsood. Solid-State Electron., **52**, 205 (2008).
[18] J. Bollmann, M. Wienecke, J. Rohrich, H. Kerkow. J. Cryst. Growth, **159**, 384 (1996).
[19] M.N. Borah, S. Chaliha, P.C. Sarmah, A. Rahman. Indian J. Pure Appl. Phys., **45**, 687 (2007).
[20] N.A. Shah, A. Nazir, W. Mahmood, W.A.A. Syed, S. Butt, Z. Ali, A. Maqsood. J. Alloys Comp., **512**, 27 (2012).
[21] D. Samanta, B. Samanta, A.K. Chaudhuri, S. Ghorai, U. Pal. Semicond. Sci. Technol., **11**, 548 (1996).
[22] S. Zhao, Y. Zhou, K. Zhao, Z. Liu, P. Han, S. Wang, W. Xiang, Z. Chen, H. Lü, B. Cheng, G. Yang. Phys. B: Condens. Matter, **373**, 154 (2006).

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