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The influence of annealing temperature on some physical properties of spray deposited nanostructured CdS thin films

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Absract. In this study, the effect of annealing temperature on physical properties of CdS thin films was studied. CdS in the form of thin film was prepared by a simple and inexpensive spray pyrolysis technique for various annealing temperatures. After deposition, films were annealed at 400-450-500 °C for 2 hours at air atmosphere. The effects of the annealing temperature on the physical properties of the films were investigated by studying the transmittance measurements, spectroscopic ellipsometry technique, atomic force microscope (AFM) observations and the four probe technique. The transmittance measurements were used to estimate the band gap energy by the linear fit of $(\alpha h\nu)^2$ curve. The band gap energy was found to be slightly decreasing with the annealing process. From the four probe measurement the resistivity was determined and found to be strongly decreasing with increasing the annealing temperature. Finally, annealing process and annealing temperature confirmed significant effects on the optical, electrical and surface properties CdS thin films.

Keywords: Annealing, CdS, thin film, AFM.

1. INTRODUCTION

In recent past, CdS is one of the most interesting II-VI semiconductors due to its interesting optical, electrical, surface and optoelectronic properties. In particular, thin films of n-type CdS are widely used as a window layer in heterojunction solar cells such as CdS/CdTe and CdS/CuInSe2 solar cells [1,2]. The properties of CdS thin films obtained by several techniques, such as sputtering [3], evaporation [4], serigraphy [5], chemical vapor deposition [6] and chemical spray [7] have generated a great amount of information about its physical properties. However, the chemical spray technique is a very low cost and simple technique that enables intentional doping and getting large area and uniform thin films [8]. In addition to this it was found that in spray-deposited films a nanolayer originates from the interface between the polycrystal-line film and the glass substrate [9]. Knowledge of the optical, electrical and surface properties of CdS films is important in many scientific, technological and industrial applications which find places in the field of optoelectronic devices, particularly solar cells. In this work we use the simple, low cost spray pyrolysis technique to deposit the thin films of CdS and the effects of annealing in air atmosphere at 400-450-500 °C. Also, the effect of the annealing temperature on the optical, electrical and surface properties of CdS films is investigated to determine the feasibility of CdS films for the solar cell applications.

2. EXPERIMENTAL

2.1. Film preparation

The spray pyrolysis experimental set up is shown in Fig. 1. CdS films were deposited on heated glass (1cm×1cm) substrates by spraying an aqueous solution. Aqueous 0.05 M $CdCl_2.H_2O$ dissolved in a mixture of methanol and deionized water (1:1), and 0.05 M $(NH_2)_2CS$ were used

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to obtain CdS films The films have been produced by spraying the aqueous solution of 0.05 M $CdCl_2.H_2O$ and 0.05 M $(NH_2)_2CS$ in a (1:1) (by volume) onto the substrates at 300±5 °C. The ultrasonic spray head to the substrate distance was approximately 30 cm. The carrier gas pressure (1 bar) and the flow rate of solution during spraying were adjusted to be 1 bar and 5 ml min^{-1}, respectively. CdS thin films were obtained from the as-grown films after an annealing process in air at 400-450-500 °C temperatures for 2 hours.

2.2. Characterization techniques

Several techniques were used for optical, electrical and surface characterization of the CdS thin films. The CdS film was deposited on glass substrates by spray pyrolysis technique using a homemade experimental setup shown in Fig. 1. Firstly, the transmission and absorption spectra of the films was measured by using a Schimadzu UV-2550 UV-VIS spectrophotometer in the range 300-900 nm and the optical energy gaps of the films were calculated using the optical method. The optical constants (refractive index and extinction coefficient) and thicknesses of films were obtained from spectroscopic ellipsometer (SE) measurements. All ellipsometric data were recorded at an incidence angle of 70° across the spectral range 300-900 nm and were analyzed using the PHE 102 Spectroscopic Ellipsometry. Latter, the resistivity values were obtained using a Keithley 2601A System SourceMeter Four-probe set up. Lastly, the surface images and roughness values of the films were determined using Park System XE 70 model atomic force microscopy (AFM).

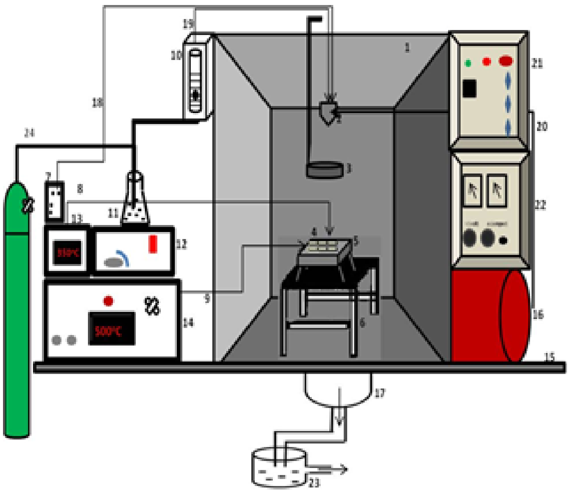

Figure 1. Spray pyrolysis set up (1) Spraying chamber, (2) Ultrasonic atomizer, (3) Moving pan (4) Glass substrates (5) Bronze block (5000-6000 Watt), (6) Moving base, (7) Oscillator, (8) 1. termocouple, (9) 2. termocouple, (10) Flowmeter, (11) Spraying solution, (12) Heater-magnetic mixer, (13) Temperature indicator, (14) Electrical heater, (15) Table, (16) Air gas, (17) Fan, (18) Cable of oscillator, (19) Spraying hose, (20) Air hose, (21) ac ampermeter (22) ac voltmeter, (23) water-filled container (24) Air tube.

3. RESULTS and DISCUSSION

3.1. Optical studies

The transmission and absorption spectra of spray- deposited CdS thin films on glass substrate were studied in wavelength 300-900 nm. The transmittance spectra of the CdS thin films as-grown and annealed were measured at room temperature and shown Fig. 2. All CdS thin films present high transparency ~70 % in the visible region from 550 to 850 nm, making the possible to be used as window layers in photovoltaic solar cells.

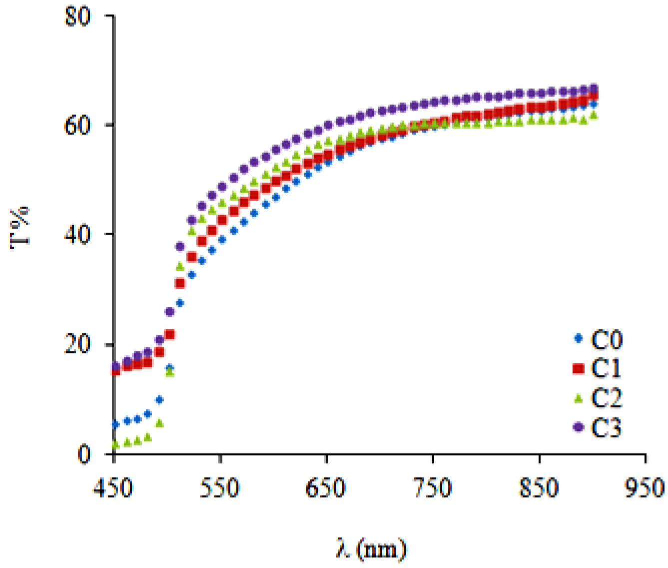

Figure 2. Transmission spectra of as-deposited and annealed CdS films.

The optical band gaps CdS thin films were calculated from the absorption spectrum. The relation between the absorption coefficient α and the incident photon energy $h\nu$ is given by eq. (1);

$$(\alpha h\nu)^2 = A\,(h\nu - E_g) \tag{1}$$

where A is a constant and E_g is the band gap energy. The optical energy gaps E_g could be obtained from the intercept of $(\alpha h\nu)^2$ vs. $h\nu$ direct allowed transitions. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ for different annealing temperatures are shown in the Fig. 3. The straight-line portion was extrapolated to the energy axis at $\alpha=0$, to obtain the band gap of CdS thin films. The optical band gap of CdS thin films was shifted from 2.43 eV to 2.34 eV. This shift to low energy values can be explained in terms of the nanosize effect of the as-deposited film. All films were found to be direct band gap materials, which is a desired property for photovoltaic solar cell applications. The variation of band gap energy with annealing temperature is depicted in Fig. 3, and it was seen that annealing caused the optical band gap values of the films to decrease.

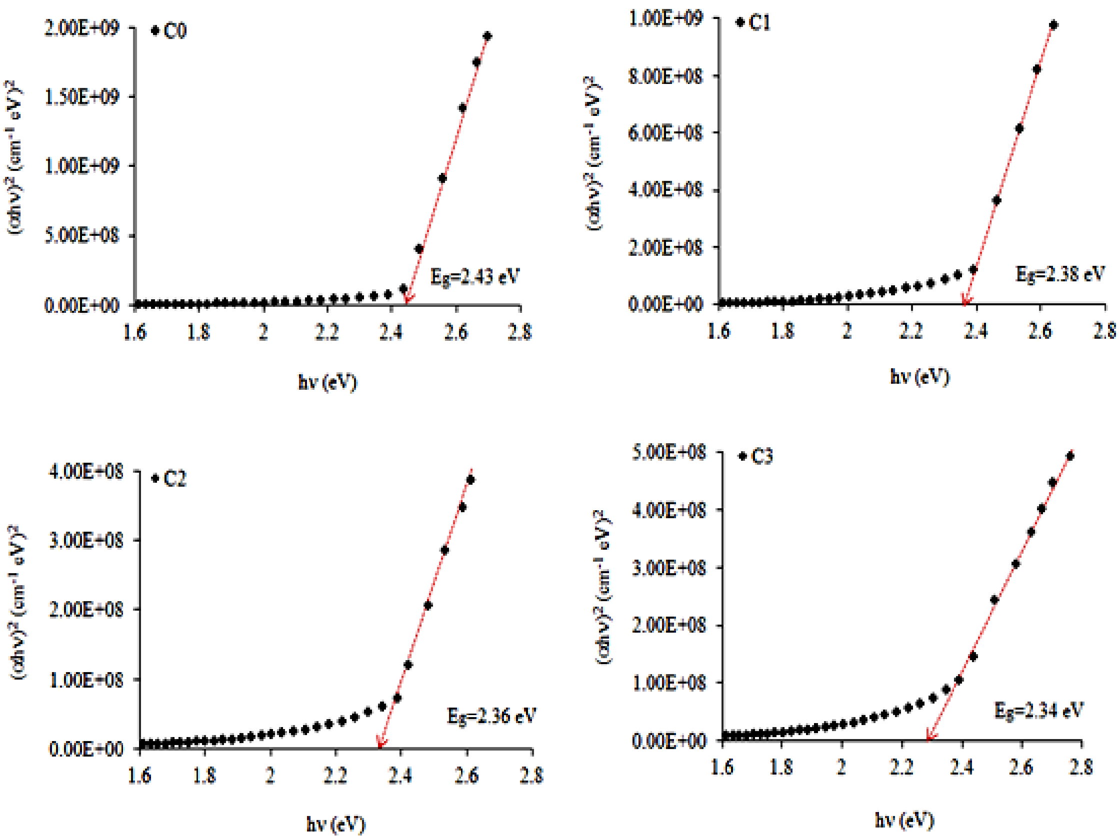

Figure 3. Variation of $(\alpha h\nu)^2$ versus $h\nu$.

SE analysis of CdS thin films allows determining the basic optical properties as film thickness (d), refractive index (n) and extinction coefficient (k). SE measurements of CdS thin films on glass substrates were carried out in air at room temperature in the wavelength range of 300–900 nm, in steps of 10 nm. The angles of incidence of the light beam on the sample surfaces were chosen to be 70° for the SE analyses. Since the CdS thin films were optically transparent in the spectral region of interest the Cauchy–Urbach (CU) dispersion model was then applied to model this region. The use of this model for transparent material was reported elsewhere [10].

In the CU dispersion model, the refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ as a function of the wavelength are given by,

$$n(\lambda) = A_n + \frac{B_n}{\lambda} + \frac{C_n}{\lambda} \qquad (2)$$

$$k(\lambda) = \alpha exp\beta\left(12400/(\frac{1}{\lambda} - \frac{1}{\gamma})\right) \qquad (3)$$

where A_n, B_n, C_n, α, β and γ are model parameters [11]. The fitted ψ spectrum, simulated with the best-fit CU model parameters, is shown by solid lines in Fig. 4. Fitting the experimental ellipsometric spectra of ψ allowed the determination of the film thickness (d), spectra of refractive index (n) and extinction coefficient (k) of all films. The thicknesses determined by fitting the experimental ellipsometric spectra and the best-fit model parameters of CdS thin films are listed in Table 1. Reflection (R) spectra of CdS films are shown in Fig. 5. It was examined that the average reflection value of CdS films is about 8 %, and this value remarkably decreases with the annealing process. Also, there is a linear variation in reflectance values with annealing process. The lowest reflectance value has been obtained for film C3. Especially, low reflectance value of C3 films makes this film a promising material for photovoltaic applications as window material or front contact. Refractive index (*n*) and extinction coefficient (*k*) spectra of CdS films are given in Fig. 6. It is clear that higher annealing temperature (especially at 450 °C and 500 °C) caused the refractive index values to decrease.

When we look at the Fig. 6, there is a little decrease in refractive index value for CdS which is annealed 2 hours. Also, refractive index values of the samples are nearly constant (~2.60–2.30) with increasing wavelength (especially from 550 nm to 950 nm). Also, at long wavelengths, extinction coefficient (*k*) values are nearly constant and similar to each other for all films. Thus, extinction coefficient (*k*) values are low between long wavelengths (550 <λ< 950 nm) and increase through short wavelengths below 550 nm. The extinction coefficient of a material is directly related to its absorption characteristic. So, at long wavelengths films would have high transmittance, low absorption and low *k* values, or vice versa for short wavelengths. Fig. 6 also shows that annealed films have higher *k* values.

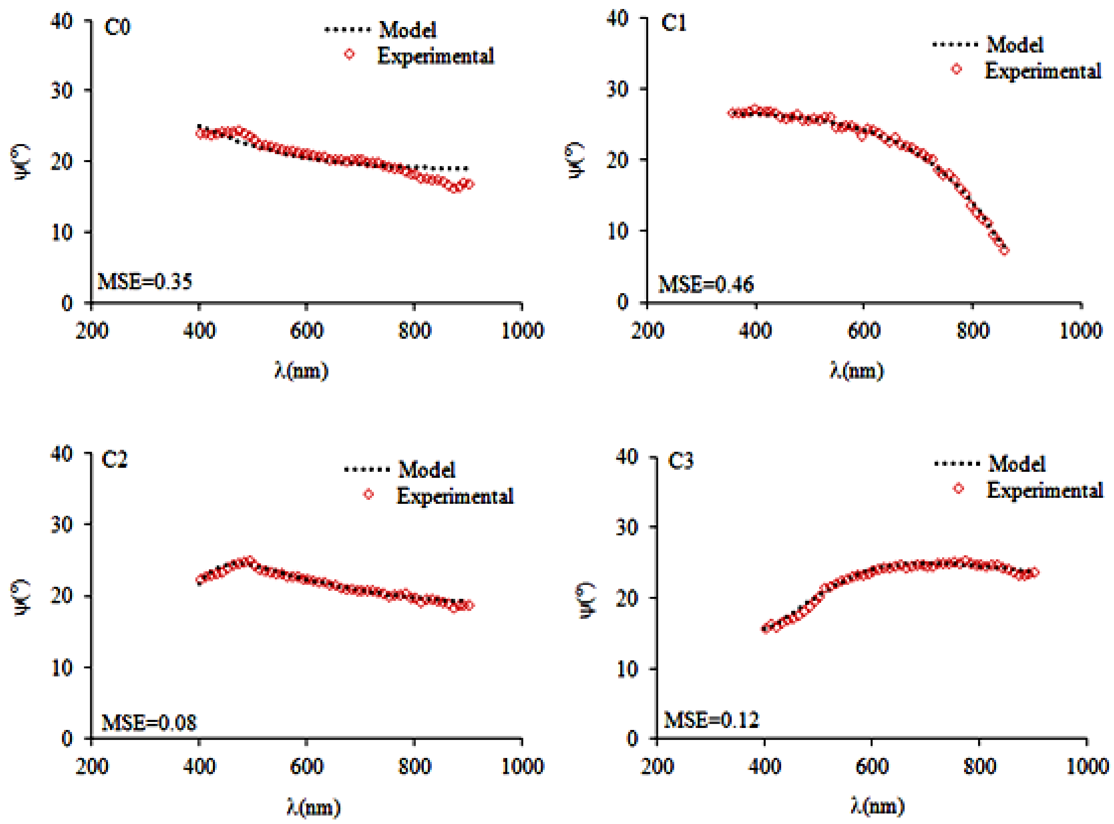

Figure 4. SE spectra of CdS thin films.

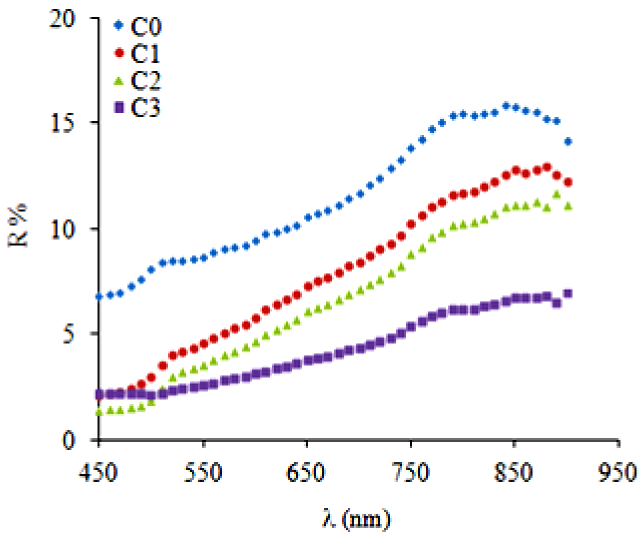

Figure 5. Reflection (R) spectra of CdS thin films.

Table 1. The thickness and SE parameters of CdS thin films.

Film	Thickness (nm)	A_n	B_n (nm)^2	C_n (nm)^4	α	β (eV)$^{-1}$	MSE
C0	180	2.32	0.028	0.022	0.075	0.044	0.09
C1	176	2.24	0.025	0.020	0.087	0.056	0.35
C2	175	2.18	0.017	0.021	0.034	0.032	0.46
C3	171	2.11	0.014	0.019	0.068	0.087	0.12

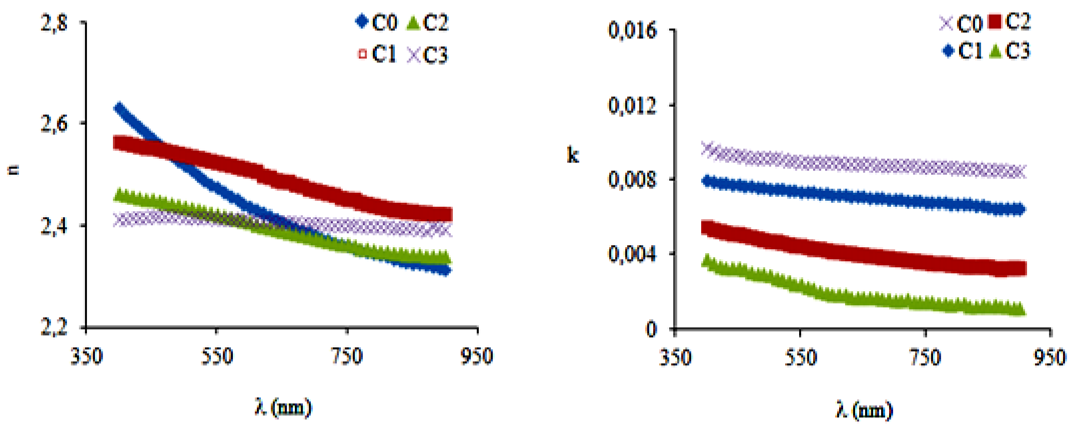

Figure 6. Refractive index (n) and extinction coefficient (k) spectra of CdS thin films.

3.2. Surface studies

AFM images of the as-deposited and annealed at various annealing temperatures CdS films are shown in Fig 7. The white patches represent the presence of material particles while the black ones represent void spaces. For all of the AFM images shown in Fig. 7, the particles dispersed in the films were of approximately spherical shapes. The larger white grains were superposed overlapping sites of CdS in the layer-by-layer deposition process. When the annealing temperature was raised, as shown in Fig. 7, the neighboring particles became more strictly connected as the vacant areas among the grains and were filled up by the relatively easier dispersal of particles in the film. Roughness values R_{pv} (peak-valley), R_q (root mean square, rms), R_a (average) of CdS thin films are given Table 2. As shown in Table 2, roughness values decrease with increasing annealing temperature. It is clear that change of annealing temperature affected the roughness values.

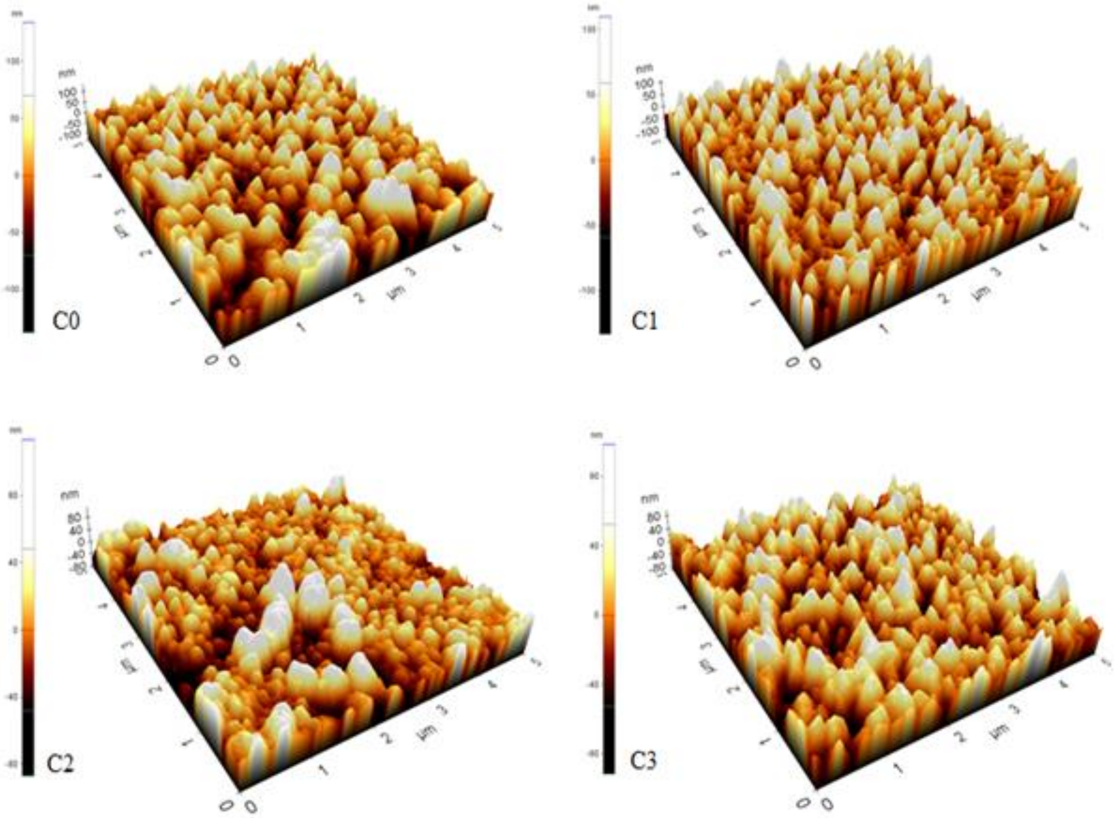

Figure 7. AFM images of CdS thin films.

Table 2. Roughness values of CdS thin films.

Film	Rpv (nm) (5×5μm2)	Rq (nm) (5×5μm2)	Ra (nm) (5×5μm2)
C0	272	36	29
C1	243	30	24
C2	200	25	19
C3	190	27	16

3.3. Electrical studies

The electrical resistivity values of CdS films were recorded at room temperature. The four probe and hot probe technique were used to find the resistivity of the CdS thin films. The change of the electrical resistivity values displayed in Fig. 8 and these resistivity values were given in Table 3. The resistivity of the films decreased from 7.96×10^4 Ωcm to 2.63×10^4 Ωcm with annealing process. Also, the films were found to be n-type as determined from the hot prope.

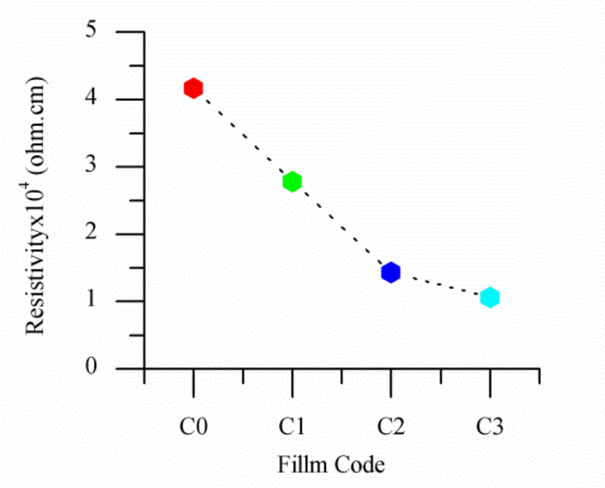

Figure 8. Electrical resistivity range of CdS thin films.

Table 3. Resistivity values of CdS thin films.

Film	$\rho \times 10^4$ (Ω.cm)
C0	4.17
C1	2.78
C2	1.43
C3	1.06

4. CONCLUSION

CdS thin films were deposited on glass substrate by spray pyrolysis technique. The effect of annealing process on optical, electrical and surface properties was studied. All the films have a high transmission ≥60 % in the UV-Vis region. The annealing treatment on the films in controlled atmospheres is useful to decrease the resistivity. The lowest resistivity value was 1.06×10^4 Ωcm for the films annealed at 500 °C. Low resistivity, suitable optical transmittance and optical band gap make these films suitable for optoelectronic and photovoltaic applications.

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