

Structural, optical and electrical properties of CdS thin films obtained by spray pyrolysis

C. Santiago Tepantlán

*Universidad Politécnica de Tulancingo,
Calle Ingenierías 100 Huapalcalco, 43629, Tulancingo, Hidalgo, México,
e-mail: cesar_upt@yahoo.com.mx*

A.M. Pérez González and I. Valeriano Arreola

*Universidad Popular Autónoma del Estado de Puebla (UPAEP),
21 Sur 1103 Colonia Santiago, 72160, Puebla, Puebla, México,
e-mail: arllenemariana.perez@upaep.mx, iracema.valeriano@upaep.mx*

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Cadmium sulphide (CdS) thin films were prepared by means of the chemical spray pyrolysis technique. The substrate temperature was varied in the range from 200 to 400°C. The structural properties of the semiconductor were characterized by X-ray diffraction; XRD patterns indicated the presence of single-phase hexagonal CdS. Direct band gap values of 2.37–2.41 eV were obtained. The refractive index is reported on depending on the substrate temperature, and was obtained from transmission spectra and from spectroellipsometry measurements. As a consequence, the optical parameters of the films were determined using the Swanepoel, Cauchy, Sellmeier and Wemple models. The resistivity of the films was found to vary in the range 10^3 – $10^5 \Omega \cdot \text{cm}$, depending on the substrate temperature.

Keywords: CdS thin films; spray pyrolysis; structural properties; optical properties; electrical properties.

Películas delgadas de sulfuro de cadmio han sido preparadas por el método químico de rocío pirolítico, variando la temperatura del sustrato en el intervalo de 200 a 400°C. Las propiedades estructurales del material obtenido fueron estudiadas utilizando la técnica de difracción de rayos X, y los patrones de difracción muestran la presencia de la fase hexagonal del CdS. Se obtuvo un ancho de banda entre 2.37 y 2.41 eV, en función de la temperatura de depósito. Las curvas de índice de refracción fueron obtenidas a partir del espectro de transmisión y por mediciones espectroelipsométricas, de manera que los parámetros ópticos fueron obtenidos usando los modelos de Swanepoel, Cauchy, Sellmeier y Wemple. La resistividad eléctrica en condiciones de oscuridad varió en el rango de 10^3 – $10^5 \Omega \cdot \text{cm}$, dependiendo de la temperatura del sustrato. Un análisis de los efectos del método de depósito en las propiedades de las películas es presentado.

Descriptores: Sulfuro de cadmio; rocío pirolítico; propiedades estructurales; propiedades ópticas; propiedades eléctricas.

PACS: 61.10.Nz; 71.55.Gs; 78.20.Ci; 78.66.-w; 78.66.Hf

1. Introduction

CdS thin films are regarded as one of the most promising materials for heterojunction thin film solar cells. Wide band CdS ($E_g = 2.42$ eV) has been used as the window material together with several semiconductors such as CdTe, Cu_2S and InP with 14–16% efficiency [1–3]. However, due to the high cost of this material, studies were developed towards polycrystalline compound semiconductors and particularly thin polycrystalline films.

The deposition of CdS films has been explored by different techniques: sputtering, thermal evaporation, chemical bath deposition, and molecular beam epitaxy [4–8]; in each of these methods polycrystalline, uniform and hard films are obtained, and their electrical properties are very sensitive to the method of preparation. Spray pyrolysis [9,10] although it is expensive, requires the use of sophisticated materials for large areas of deposition, now gives good quality semiconductors which permit the fabrication of solar cells with satisfactory efficiency.

The aim of this work is to produce CdS thin films by means of the spray pyrolysis technique and to investigate their structural, optical and electrical properties, and this de-

pendence on substrate temperature. Optical properties were obtained from transmission spectra (TS) and Spectroellipsometry (SE) measurements.

2. Experimental

The spray pyrolysis technique is a simple technology in which an ionic solution containing the constituent elements of a compound in the form of soluble salts is sprayed onto over-heated substrates using a stream of clean, dry air. The apparatus used for our sprayed process is diagrammed in Fig. 1, and has been described in Ref. 11. The CdS thin films were prepared by spraying an aqueous solution of cadmium chloride (CdCl_2) and thiourea [$\text{CS}(\text{NH}_2)_2$] on a glass substrate kept at 200, 300 and 400°C. The atomization of the chemical solution into a spray of fine droplets is effected by the spray nozzle, with the help of compressed air as the carrier gas. The spray rate of about $10 \text{ cm}^3/\text{min}$ through the nozzle ensures a uniform film thickness. The substrates are Corning 1737 glass 2×2 cm, and are placed in a fitted socket at the surface of a substrate heater when sprayed. The heater is a cylindrical stainless steel block furnace, electrically controlled to an accuracy of $\pm 1^\circ\text{C}$. The substrate temperature was varied, while the other spray parameters were kept constant.

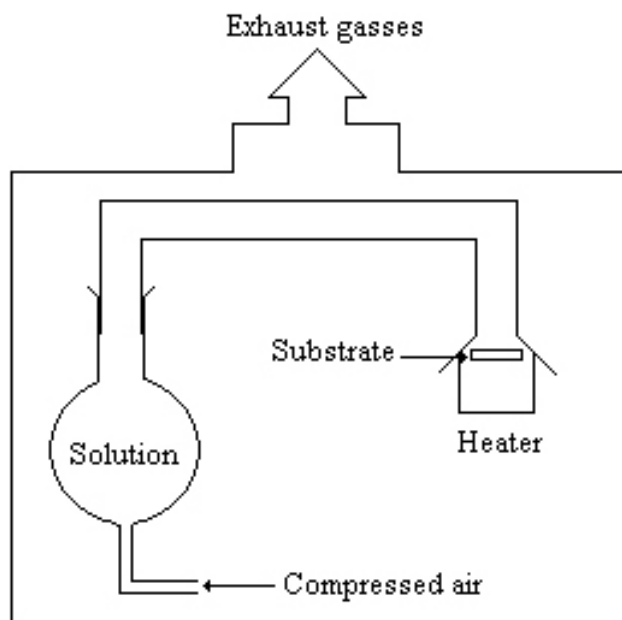


FIGURE 1. Schematic diagram of the spraying apparatus.

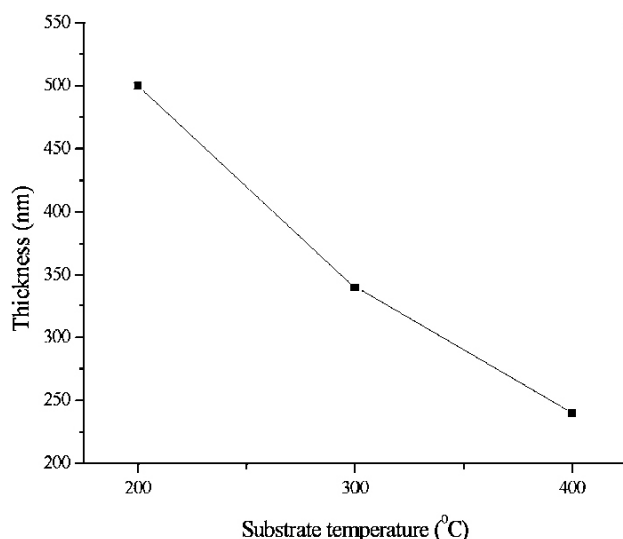


FIGURE 2. Effect of substrate temperature on thickness of CdS films.

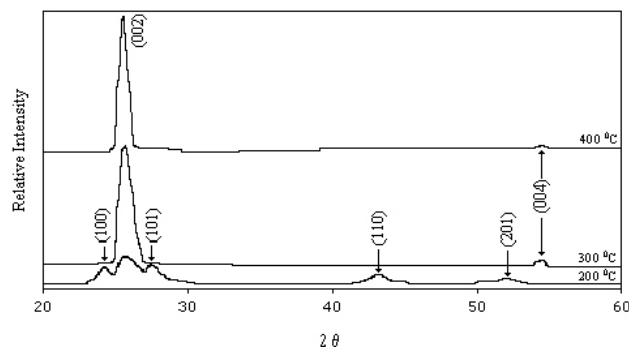


FIGURE 3. X-ray diffractograms of CdS films with different substrate temperature.

The film thickness was measured by a contact profilometer (Tencor Instrument 200) with an experimental error of $\pm 2\%$.

The X-ray diffraction patterns of the films were recorded with a JEOL 60 PA X-ray diffractometer operating with a 0.15418 nm monochromatized Cu k_{α} radiation at 40 kV and 30 mA with Ni filter.

Transmission T spectra of the prepared samples were measured by normal incidence of light using a Spectronic Unicam model UV300 double-beam spectrophotometer, in the wavelength range 300–900 nm, using a blank substrate as the reference position. Thus, we obtained the optical absorption edge, the refractive index n , the film thickness d and the optical gap E_g . We define the optical gap as E_{04} , i.e., the energy at which the optical absorption coefficient is equal to 10^4 cm^{-1} [12]. At maximum transmission, we get the position and order of the interference fringes in a non-absorbing region of the spectra. Then, we fit to a parabolic expression for n as a function of energy using an assumed approximate film thickness. The measured asymptotic transmission is used to scale the deduced value of n and to provide the correct film thickness, which is compared with that measured by the profilometer. These values were used in the calculation of the optical absorption coefficient α , using standard formulae [13].

The film thickness, the dispersion of the refractive index and the optical gap were determined using spectroscopic ellipsometry for a spectrum wavelength range of 300 to 800 nm. All SE measurements were taken at an incidence angle of 60 deg.

The dark electrical resistivity of the prepared films was measured by the Van der Pauw four-probe method. The potential difference V and current I were determined using a conventional D.C. technique.

3. Results and Discussion

3.1. Structural properties

Figure 2 shows the variation in thickness with the substrate temperature; the decrease in film thickness is due to a decrease in the deposition rate of the initial specimens with an increasing temperature.

Diffractograms of films produced at different substrate temperatures (200, 300 and 400°C) are shown in Fig. 3. XRD analysis showed that the films have highly oriented crystallites, with the classical hexagonal structure or wurtzite type, with a preferential orientation along the c-axis, (002) direction perpendicular to the substrate plane. This behavior is more intense for samples obtained at 300 and 400°C, where the peak at 26.8° is the only one present.

The degree of preferred orientation increased with the substrate temperature. Thus, the film prepared at the highest temperature has a better crystalline quality, as indicated from its XRD spectra.

The average grain size was calculated from the Scherrer formulae, which involve the width of the X-ray diffraction line [14]:

$$G = \frac{0.9\lambda}{D \cos \Theta}, \tag{1}$$

where Θ is the diffraction angle, λ is the wavelength of the X-ray source and D is measured in radians as full-width at half maximum of the diffraction line. The results obtained are shown in Fig. 4. The grain size was found to increase with an increasing substrate temperature, which is the same behavior as that reported by Ashour, in Ref. 10, for spray-pyrolysed CdS thin films. Thus, increasing the substrate temperature decreases the density of the nucleation centers and under these circumstances, a smaller number of centers start to grow, resulting in large grains.

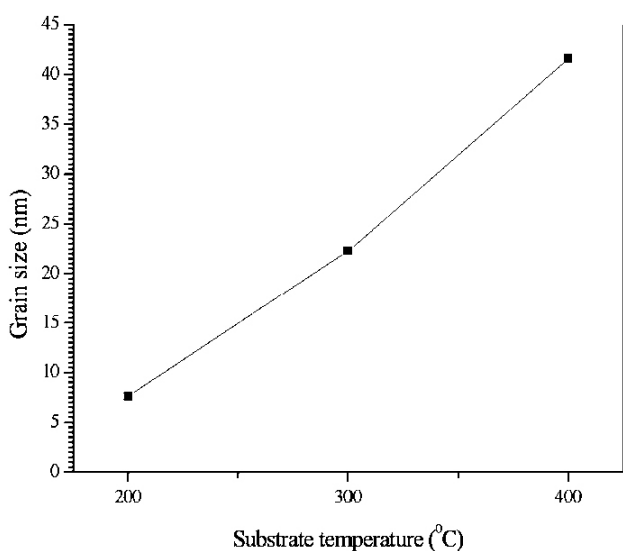


FIGURE 4. Effect of substrate temperature on grain size of CdS films.

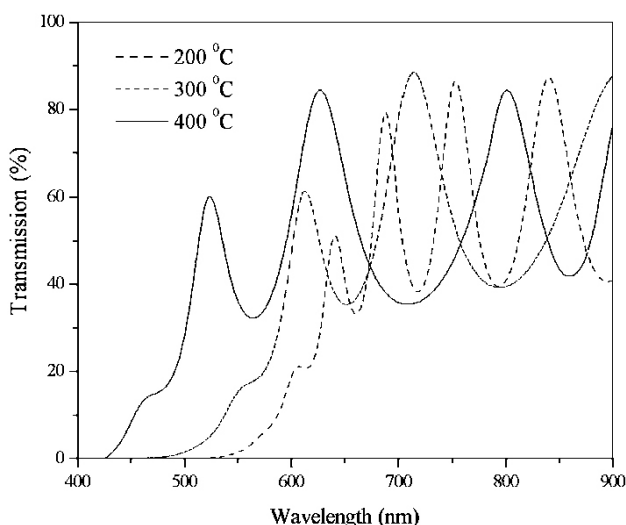


FIGURE 5. Transmission spectra for CdS thin films.

3.2. Optical properties

3.2.1. Transmittance spectrum measurement

Figure 5 shows plots of transmission spectra versus wavelength for the films studied. The transmission coefficient strongly depends on the film structure, which is determined by the preparation methods, film thickness and deposition conditions.

The number of interference fringes in the transmission curve (see Fig. 5) is determined by the thickness of the film. The refractive index in the spectral domain of the medium and strong transmission is calculated using the Swanepoel model [13] by creating smooth envelopes, from the interference of maxima and minima, of the form $y = c_1 + (c_2 + c_3x)^{1/2}$. The refractive index is first approximated by [15]:

$$n = \left[N + (N^2 - n_s^2)^{1/2} \right]^{1/2}, \tag{2}$$

where

$$N = 2n_s \frac{T_{max} - T_{min}}{T_{max}T_{min}} + \frac{2n_s^2 + 1}{2}. \tag{3}$$

In this expression, T_{max} and T_{min} are the maximum and the minimum transmission at the same wavelength, one being measured and the other calculated from the envelope function.

The refractive index of the glass substrate n_s is determined by

$$n_s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1 \right)^{1/2}, \tag{4}$$

where T_s is the substrate optical transmission. By using n_s as the refractive index of the film, the order m at both extremes of the transmission curve can be determined by the interference fringe equation

$$2nd = m\lambda, \tag{5}$$

where d is the thickness of the film. The m values are rounded to the nearest integer or half integer. Then, with these values and Eq. (5), we determine the refractive index n , which is plotted in Fig. 6. The refractive index decreases with the substrate temperature, when the crystalline quality is better and the crystallite size is increasing.

At the absorption edge, the absorption coefficient can be calculated using the expression:

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right). \tag{6}$$

According to Ashour [10,11] the optical gap can be determined from values of $\alpha(\delta)$ in the region of medium absorption, using the expression:

$$\alpha = \frac{B (h\nu - E_g)^{1/2}}{h\nu}, \tag{7}$$

where B is a constant, $h\nu$ is the photon energy, in eV, and $n=1$ for a direct-gap material and $n=4$ for an indirect-gap material. Then by plotting $(\alpha h\nu)^2$ versus $h\nu$ is possible to obtain

the direct optical gap from extrapolation of the lineal portion of the plot to the energy axis. The optical gap for the samples studied varies from 2.37 to 2.41 (see Fig. 7), which is in agreement with the value reported by other authors [6,11,16].

3.2.2. Spectroellipsometry measurement

The optical gap and the refractive index can be obtained from spectroellipsometry measurements; in Fig. 8, dispersion curves measured by the ellipsometric technique are shown; ten curves were measured in each case and a medium value is reported.

We studied the spectral dispersion of the refractive index for CdS samples. The dispersion spectrum of the refractive index was fitted using the Cauchy formula [17]:

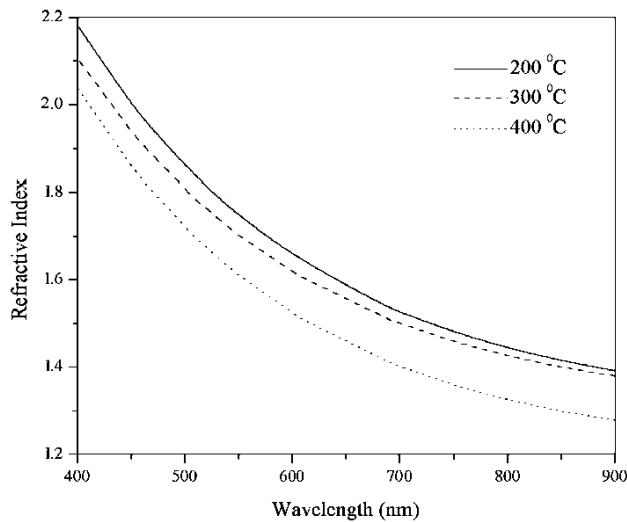


FIGURE 6. Refractive index of CdS films obtained with different temperatures.

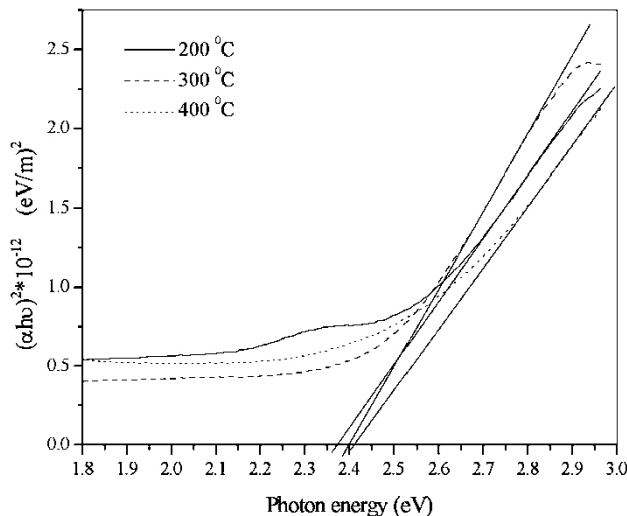


FIGURE 7. Variation of $(\alpha h\nu)^2$ with photon energy and optical gap for CdS films obtained with different temperatures.

TABLE I. Cauchy parameters and the fit quality.

T (°C)	α	$\beta(10^{-2})$	χ^2
200	1.64	0.44	3.2×10^{-6}
300	1.49	0.48	2.1×10^{-6}
400	1.39	0.52	3.9×10^{-6}

TABLE II. Sellmeier constants for CdS thin films.

T (°C)	A	B*(10 ⁻²)	n_∞	B*10 ⁻² (from (12))
200	1.722	0.968	1.65	0.949
300	1.250	0.946	1.50	0.925
400	0.742	0.931	1.32	0.918

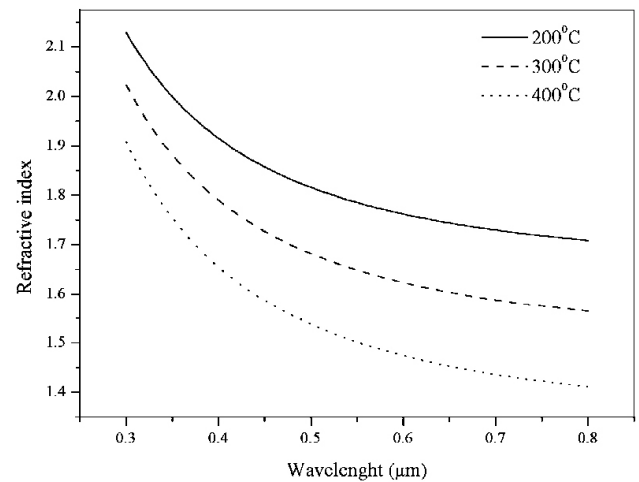


FIGURE 8. Dispersion curves measured by ellipsometry.

$$n = \alpha + \frac{\beta}{\lambda^2}, \quad (8)$$

where, α and β are the Cauchy's parameters and λ is the wavelength of light used at SE. For $\lambda \rightarrow \infty$, the significance of the α parameters appears immediately as n_∞ . The values of the fit parameters and the fit quality parameter χ^2 are presented in Table I.

Another model used in the refractive index dispersion study is the Sellmeier' model [6], gives:

$$n^2 = 1 + \frac{A\lambda^2}{\lambda^2 - B}, \quad (9)$$

where A and B are the Sellmeier parameters. Under these conditions we can see that $n_\infty = \sqrt{1 + A}$, and the calculated values are given in Table II. Comparing these values with the α values from Table I, we find good agreement.

Wemple and Di Domenico [18] have developed a model where the refractive index dispersion is studied in the region of transparency below the gap, using the single-oscillator approximation. Defining two parameters, the oscillation energy

E_0 , and the dispersion energy E_d , this model concludes that:

$$n^2(\omega) - 1 \cong \frac{E_d E_0}{E_0^2 - E^2}, \quad (10)$$

Both Wemple parameters can be obtained from the slope and the intercept with the y-axis of the plot, $1/(n^2-1)=f(E^2)$. The energy oscillation and dispersion energy values are given in Table III. The dispersion energy measures the average strength of interband optical transitions. Wemple and Di Domenico have related this parameter to the coordination number of the anion and the number of valence electrons per anion. The oscillator energy is related by an empirical formula to the optical gap value: $E_o = 1.7E_g$ [12,19]. The calculated values of the optical gap are also presented in Table II. We can see that a higher deposition temperature means a higher optical gap value. This result is very important because it shows that the refractive index and the optical gap of the material can be controlled by the deposition conditions.

Applying Sellmeier's model and Wemple's model on the same photon energy range, the A and B parameters can be expressed as

$$A = \frac{E_d}{E_0} \quad (11)$$

$$B = \frac{h^2 c^2}{E_0^2}, \quad (12)$$

where h is the Plank's constant and c is the speed of light in a vacuum.

We calculated the B parameter values using (12), and the results are given in Table II. A comparison between the third and the fifth columns shows good agreement between the two optical models.

We have correlated the optical film's two parameters with each other; as is known, when the refractive index decreases, the value of the optical gap increases. On the other hand, a lower deposition temperature means higher optical gap values.

3.3. Electrical properties

The resistivity was measured at room temperature in dark conditions. Figure 9 shows the variations in resistivity with the substrate temperature. All films exhibit semiconducting behaviors with resistivity in the range of 10^3 - $10^5 \Omega \cdot \text{cm}$, decreasing with substrate temperature. This decrease is attributed to the growth in grain size and the improvement

TABLE III. Optical gap and Wemple Di Domenico parameters for CdS thin films.

T ($^{\circ}\text{C}$)	E_d (eV)	E_0 (eV)	E_g (eV)
200	6.96	4.046	2.38
300	5.12	4.097	2.41
400	3.05	4.114	2.42

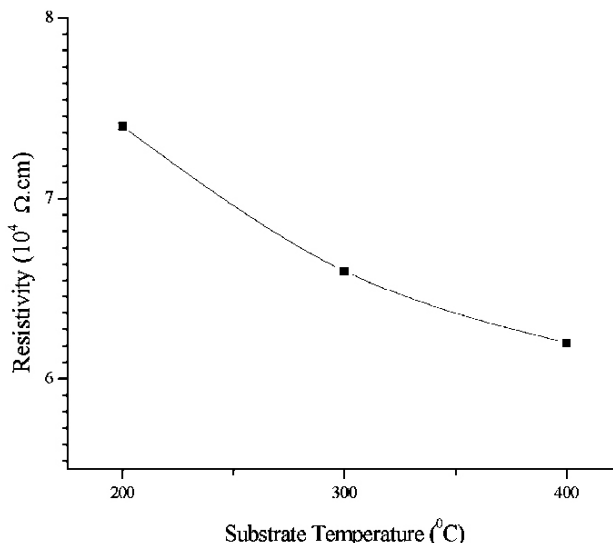


FIGURE 9. Effect of substrate temperature on resistivity of CdS films.

in film stoichiometry, as is indicated by the XRD patterns. The results obtained are similar to those obtained by other authors [6,13,19].

4. Conclusions

The content of this paper can be summarized by the following statements:

1. CdS films were fabricated by spray pyrolysis using a solution of cadmium chloride and thiourea.
2. The films prepared at the lowest temperature have the least crystalline quality and the greatest thickness, as was observed in XRD patterns.
3. Optical properties of CdS thin films were studied using transmittance spectra and spectroellipsometry.
4. Refractive index and optical gap were calculated using Swanepoel's model of transmittance spectra.
5. The normal dispersion of the refractive index was successfully fitted with the Cauchy, Sellmeier and Wemple *et al.* formula, and good agreement between the models is observed.
6. The optical gap and the dispersion energy values were determined using the Wemple and Di Domenico approximation.
7. The calculated values of the optical gap shown good agreement between the used models.
8. The optical gap and oscillator energy rise, while the oscillator strength falls, with an increase in the deposition temperature.

9. The refractive index and the optical gap of the material can be controlled by the deposition conditions.
10. The electrical resistivity ranged from 10^3 - $10^5 \Omega \cdot \text{cm}$, varying with the substrate temperature.

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