Influence of Substrate Temperature on the Optical Properties of Nano Crystalline $CdIn_2Se_4$ thin Films

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$CdIn_2Se_4$ thin films were prepared by a thermal evaporation technique on glass and quartz substrates. The influence of substrate temperature on the structural and optical properties has been studied. The crystal structure and orientation of the prepared films were investigated by x-ray diffraction and observed that $CdIn_2Se_4$ corresponds to cubic crystal structure. The variation in crystallite size with substrate temperature were studied and observed an increase in crystallite size with substrate temperature.

The optical constants were calculated in the spectral range 600 - 2500 nm from the transmittance and the reflectance data using Merman's exact equations. The absorption spectra have been taken in the wavelength range 600 nm to 1000 nm. The direct band gap of thin films was calculated from absorption spectra, which reveals that band gap increases as the substrate temperature increases which may be attributed to the increase in the crystallite size. The dispersion parameters such as oscillator energy, dispersion energy, dielectric constant, bond enrgy and the free charge concentration were also estimated.

1. Introduction

Cadmium indium selenide ($CdIn_2Se_4$) is the semiconducting ternary chalcogenide of the type $A^{II} B^{III} X_4$ where A = Cd, Zn or Hg, B = In or Ga, and X = S, Se or Te. The ternary chalcogenides have potential applications in optoelectronic devices, in non-linear optics [1] and in solar energy conversion due to their interesting tailored properties [2-4]. $CdIn_2Se_4$ is promising in optoelectronic applications and solar cells [5] due to its high absorption coefficient in the visible. $CdIn_2Se_4$ thin films have been prepared by different techniques [6,7]. The optical properties of single crystals were studied in the fundamental absorption region using polarized light and the width of the forbidden band gap was found to be 1.82 eV [8]. $CdIn_2Se_4$ is a direct band gap semiconductor with an energy gap of 1.73 eV which make it interesting for solar cells[4,9]. The optical properties of $CdIn_2Se_4$ films have been studied [10-14] and the effect of temperature on their optical properties have been reported [15,16].The aim of the present work is (i) to prepare of $CdIn_2Se_4$ in the nano-crystalline structure (ii) to the investigate the effect of nano size on the optical properties through the change of both the substrate temperature.

2. Experimental Techniques

$CdIn_2Se_4$ thin films of different thickness (100 nm – 500 nm) were deposited on a pre-cleaned quartz and glass substrates with the help of a high vacuum-coating unit (Edwards type E306A) worked at 10^{-5} Torr. Pure (99.999%) bulk $CdIn_2Se_4$ was used to deposit the thin films with deposition rate equals to 7nms^{-1}. The substrate temperature was varied from 298 K to 523 K. Thin tantalum boat was used as source heater. The film thickness was measured by Tolansky's method [17]. Also the rate of deposition and the films thickness were controlled using a quartz crystal thickness monitor (Model FTM4, Edwards co, England). X-ray diffractometer (Philips PW 3710BASED), using $Cu_{K\alpha}$ radiation operating at 40 kV and 30 mA was used to investigate the structure properties. The transmittance, T, and reflectance, R, of the films deposited on quartz substrates were determined at normal incidence in the wavelength, range λ = 600-2500 nm by means of a double-beam spectrophotometer (JASCO 570) attached to a specular reflection stage.

From the measured values of T_{exp} , R_{exp} and film thickness d, the values of the refractive index n, and the absorption index k, were computed by a special computer program [18-20] based on minimizing $(\Delta T)^2$ and $(\Delta R)^2$ simultaneously, where

$$(\Delta T)^2 = |T_{(n,k)} - T_{exp}|^2 \quad (1)$$

$$(\Delta R)^2 = |R_{(n,k)} - R_{exp}|^2 \quad (2)$$

where $T_{(n,k)}$ and $R_{(n,k)}$ are the values of T and R, calculated by using Murmann's exact equations[21]. By taking into account the experimental error in measuring the film thickness to be ± 2.6 % and in T_{exp} and R_{exp} to be ± 1%, the errors in the calculated values of n and k were estimated to be ± 3 and ± 2.5 %, respectively.

3. Results and Discussions

3.1.Structural Characterization

Figure (1) shows the XRD pattern of $CdIn_2Se_4$ thin films deposited by thermal evaporation technique on glass substrates at different substrate temperatures. The diffraction pattern revealed that the $CdIn_2Se_4$ films correspond to cubic crystal structure. The intensity of the diffraction peaks was found to increase and to shift slightly towards higher values as the substrate temperature increases from 298 to 580K. For the cubic lattice parameters evaluation, we have used the quadratic relation:

$$d_{hkl} = a/[h^2+k^2+l^2]^{1/2} \quad (3)$$

where (h, k, l) are the Miller indices of reflecting planes appearing on the diffraction spectrum and $d_{h,k,l}$ is the spacing between adjacent planes. The calculated lattice parameter (a) and the unit cell volume ($V = a^3$) reveled that the unit cell volume decreases as the substrate temperature increases. The lattice constant value is 5.83Å at 298K, 5.81Å at 460K and 5.77Å at 580K in agreement with the standard values of *JCPDS* data card [22,23]. The crystallite size of the films was determined using Scherer's formula [24].

$$D = k\lambda\ (\beta_{2\theta} \cos\theta)^{-1} \quad (4)$$

where $k = 0.9$ is the shape factor, λ is the wavelength of the x-rays, β is the full width at half maximum (FWHM) and θ is the Bragg's angle. It is found that the crystallite size increases with substrate temperature. It ranges between 17.81 nm and 24.75 nm as the substrate temperature varies between 298K and 580K.

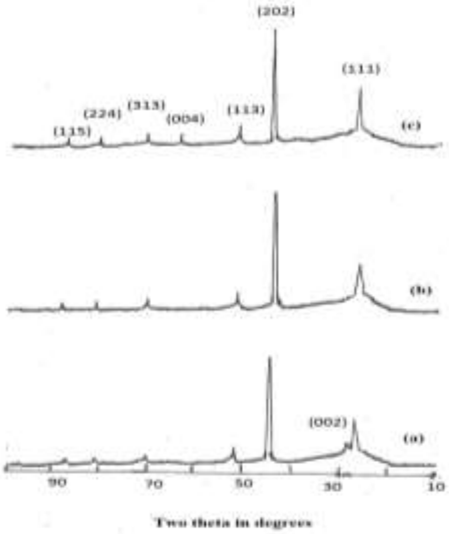

Fig.(1): XRD patterns of $CdIn_2Se_4$ films with thickness 450 nm at a) 298 K , b) 460 K and c) 580K.

3.2. Optical properties

3.2.1 Spectral distribution of the transmittance T and the reflectance R of $CdIn_2Se_4$ thin films

Figure (2) shows the transmittance *T* and the reflectance *R* for $CdIn_2Se_4$ films deposited at 298 K with different thicknesses as representative example. It is found that the spectral distributions *T(λ)* and *R(λ)* at longer wavelengths with respect to the absorption edge that $CdIn_2Se_4$ films become transparent and $T+R=1$ indicated no light is scattered.

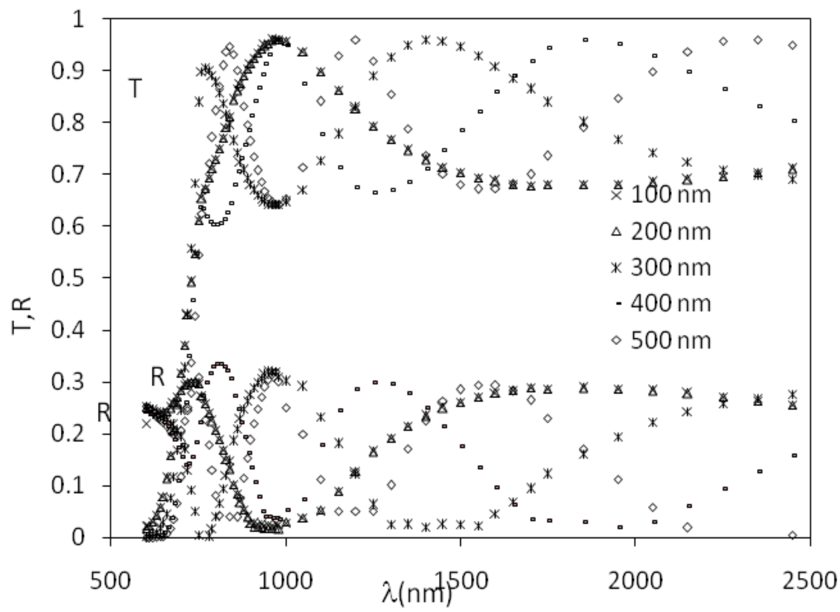

Fig.(2): Transmission, *T*, and reflection, R, spectra of $CdIn_2Se_4$ thin films of different film thicknesses prepared at 298 K.

The effect of the substrate temperature on the optical constants of $CdIn_2Se_4$ thin films were carried out at different substrate temperatures 298, 350, 360, 460, 550 and 580°K. Fig.(3) shows transmission spectra of $CdIn_2Se_4$ thin films (450nm) as a function of wavelength at different substrate temperatures in the spectral-range of 600 – 2500 nm. It is clear that the transmittance *T* shifted toward longer energy as the substrate temperatures increased, this indicated that the energy gap increased with increasing the substrate temperatures this due to the increased of the particles size as proved by structural studies.

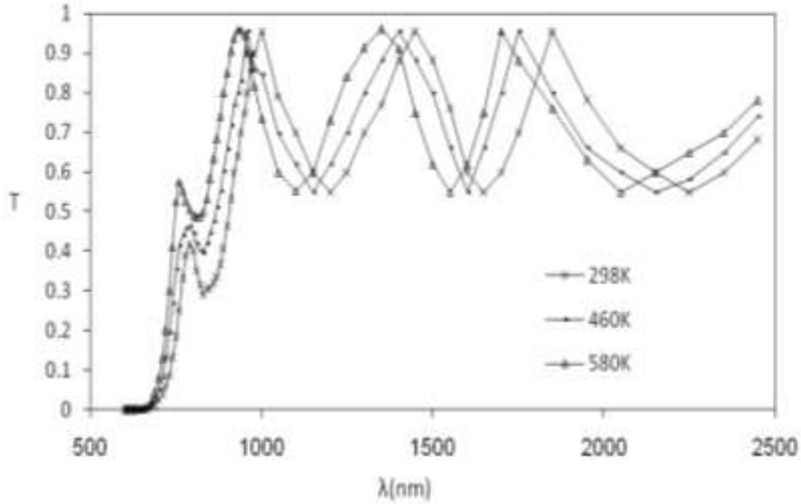

Fig.(3): Transmission spectra of *$CdIn_2Se_4$* thin films (450 nm) as a function of wavelength at different substrate temperatures (298 K, 460 K and 580 K as representative example).

3.2.2. The spectral distribution of the absorption spectra of $CdIn_2Se_4$ thin films.

The mean values of optical absorption spectra for *$CdIn_2Se_4$* thin films at different substrate temperature are shown in Fig. (4).

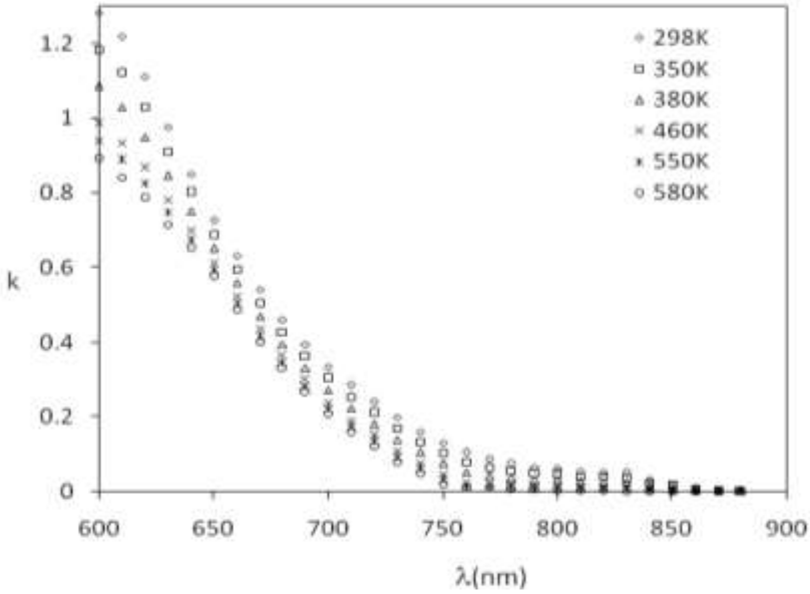

Fig.(4): The mean values of absorption spectra of $CdIn_2Se_4$ thin films with different substrate temperature

For the direct band-gap semiconductor, the relation between the absorption edge and photon energy (*hν*) can be written as follows [25]:

$$\alpha h\nu = A\,(h\nu - E_g^{opt})^{1/2} \qquad (5)$$

where α is the absorption coefficient, A is a constant, h is Planck's constant, ν is the photon frequency and Eg is the optical band gap. The plot of $(\alpha h\nu)^2$ versus hν at different substrate temperature is shown in Figure (5). An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ on the y-axis versus photon energy (hν) on the x-axis gives the value of the optical band gap E_g. The variation of band gap with substrate temperature is given in Table 1. Typically band gap increases from 1.82 to 1.87 eV because the particle size increases. This confirms the effect of the substrate temperature on the density of localized states and microstructure of the tested films [26,27].

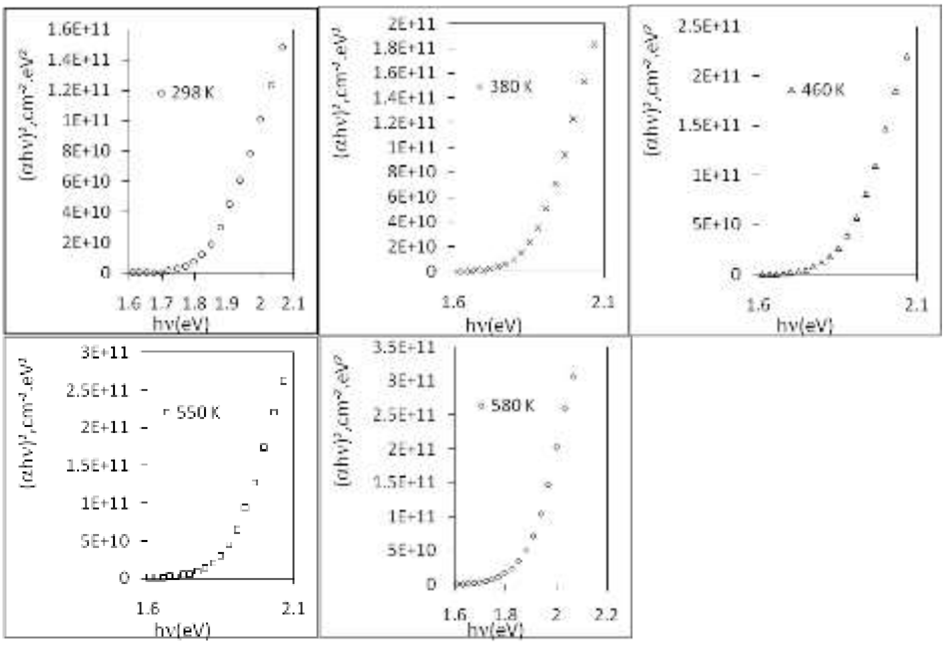

Fig.(5): Plot of $(\alpha h\nu)^2$ versus hυ with different substrate temperatures.

3.2.3. ***The dispersion parameters of $CdIn_2Se_4$thin films of $CdIn_2Se_4$ thin films***

The mean values of spectral distributions *n(λ)* for $CdIn_2Se_4$ films of different thicknesses at different substrate temperature were illustrated in Fig.(6). From Fig.(4) and Fig.(6) one can conclude that the optical constants *n* and *k* are affected by substrate temperatures and they independent on the film thickness.

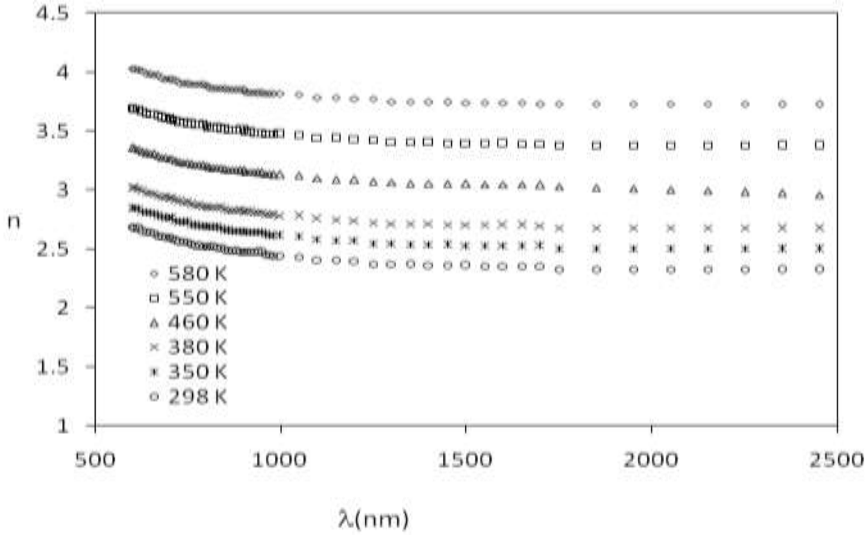

Fig.(6): Plot of refractive index, n versus λ for $CdIn_2Se_4$ thin films with different substrate temperatures

The real dielectric constant ε_1 $(=n^2-k^2)$ can be represented by the formula[28,29]:

$$\varepsilon_1 = \varepsilon_L - B\lambda^2 \quad (6)$$

where, ε_L is the lattice dielectric constant, B is a constant and λ the wavelength at which $\boldsymbol{\varepsilon_1}$ is calculated. Fig.(7) shows ε_1 as a function of λ^2 for $CdIn_2Se_4$ thin films of different substrate temperatures. It yield straight lines.

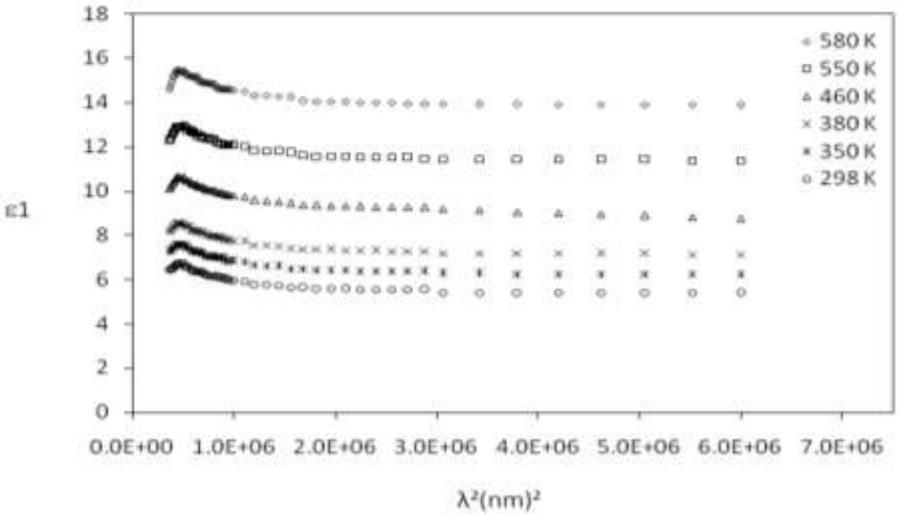

Fig.(7): *Plot of* ε_1 versus λ^2 for $CdIn_2Se_4$ thin films deposited at different substrate temperatures.

The extrapolation of this line to intersect with the Y-axis yields ε_L. As shown ε_L for $CdIn_2Se_4$ films deposited at 298 K equal 5.836. It is clearly that ε_L of $CdIn_2Se_4$ increased with substrate temperature as shown in table 1. The slope of the given straight line is *B*, it is given by:

$$B = e^2N/4\pi\varepsilon_o m^*c^2 \tag{7}$$

where *e* is the charge of the electron (1.6 x 10^{-19} coulomb), *N* the free charge carrier concentration, ε_o the vacuum permittivity (8.85 x 10^{-12} Fm^{-1}), c is the speed of light ($3x10^{10} ms^{-1}$)and m^* is the effective mass of the electron ($0.15m_o$[30].

Therefore knowing the slope, *N* the free charge carrier concentration can be calculated. It was found in the order of $11.2x10^{20} m^{-3}$ at 298 K and $1.6x10^{20} m^{-3}$ at 580 K.

Rrefractive - index, n dispersion data below the inter band absorption edge –effective oscillator can be fit to the Wemple - DiDomenico dispersion modle based on the single oscillator[28,29]:

$$(n^2 - 1)^{-1} = \frac{E_0}{E_d} - \frac{1}{E_d E_0} E^2 \tag{8}$$

On the other hand the refractive index (n_∞) at zero photon energy $(E = 0)$ is given by the expression[28,29]:

$$(n_\infty)^2 - 1 = \frac{E_d}{E_0} \tag{9}$$

where, *E* is photon energy , E_0 is the single oscillator energy and E_d is the dispersion energy. The oscillator strength is derived from the slope of the straight-line portion of the $(n^2 - 1)^{-1}$ versus, (E^2) plot. Fig.8 gives a plot of $(n^2 - 1)^{-1}$ versus, (E^2) for $CdIn_2Se_4$ thin films. As shown in Table (1), the effect of substrate temperature is clear on the values of the dispersion energy, the single oscillator energy and the free charge carrier concentration.

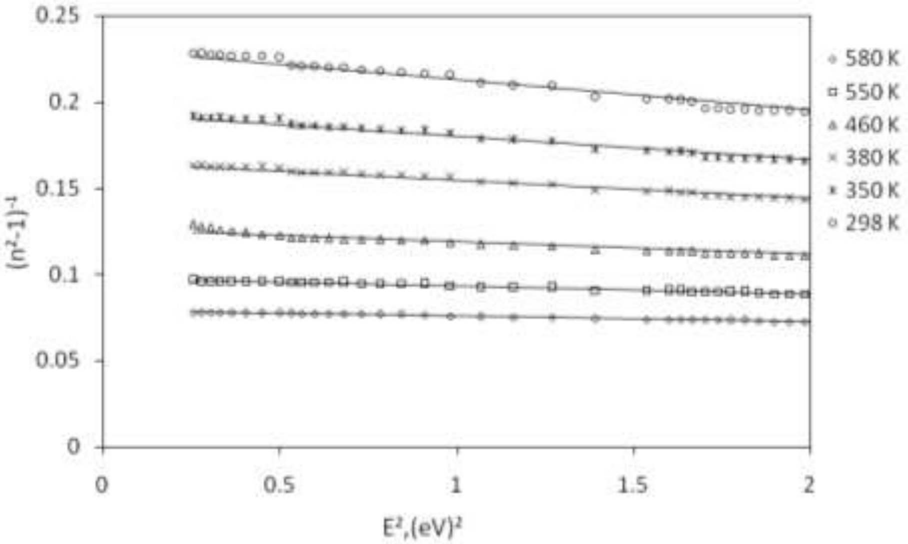

Fig.(8): Plot of $(n^2-1)^{-1}$ versus E^2 for $CdIn_2Se_4$ thin films deposited at different substrate temperatures.

Table (1): Values of energy gaps and ddispersion parameters of $CdIn_2Se_4$ thin films deposited at different substrate temperature

T_s (K)	E_g (eV)	E_d (eV)	E_o (eV)	ε_∞	B (eV)	ε_L	N $(10^{20} m^{-3})$
298	1.82	14.3	3.36	5.26	0.21	5.836	11.20
350	1.83	18.2	3.57	6.11	0.27	6.695	8.01
380	1.84	22.8	3.79	7.02	0.33	7.613	6.41
460	1.85	26.8	3.45	8.77	0.39	9.763	5.87
550	1.86	45.2	4.42	11.23	0.66	11.872	2.62
580	1.87	65.1	5.12	13.71	0.96	14.355	1.60

The dispersion energy, E_d, which is measure of the strength of inter band optical transitions, is found to obey the empirical relationship[28,29].

$$E_d = \beta N_c Z_a N_e \tag{10}$$

where β is a constant and has the value of 0.37 eV and 0.26 eV for covalent and ionic material, respectively [28,29], N_c = 4 is the coordination number of the cautions, Z_a = 2 is the formal valiancy of the anion and N_e (=8.5) is the effective number of valence electrons per anion.

4. Conclusions:

Polycrystalline $CdIn_2Se_4$ thin films of cubic phase were prepared by thermal evaporation technique on glass and quartz substrates with different substrate temperature. With the increase in substrate temperature, the diffraction intensity increases with a (202) preferred orientation. The particle size of $CdIn_2Se_4$ was changed from 17.81 nm to 24.75 nm as the temperature was changed from 298 to 580K. The band gap increases from 1.82 to 1.87eV as the substrate temperature increases from 298 to 580K. Effect of the substrate temperature on the refractive index was investigated. It was found that refractive index dispersion data obeyed the single oscillator model, from which the dispersion parameters, E_0, E_d and dielectric constant, were determined as a function of the substrate temperature.

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