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RESEARCH ARTICLE

Effect of Substrate Temperature on Optical Properties of Cu2ZnSnS4 Thin Films Preparing by Chemical Spray Pyrolysis Technique

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Abstract

The optical properties of thin films of Cu_2ZnSnS_4 have been studied by deposited on glass substrate by chemical splash spray pyrolysis method (CSP) ,with constant concentration and different substrate temperatures of (350, 400 and 450) °C. CZTS films were prepared by chemical spray pyrolysis by dissolving of copper (II) chloride ($CuCl_2$), zinc (II) Zn (CH_3COO).$2H_2O$, tin (IV) chloride ($SnCl_4$), and Thiourea (CS $(NH_2)_2$,were utilized as sources of Copper particles, Zinc particles, Tin particles and Sulfur particles individually. The UV-Vis study showed high optical absorption coefficient and wide direct band gap for solar region. Further the optical constants such as refractive index, extinction coefficient and dielectric constant have been calculated for all samples. The optical energy gap for permitted direct electronic progress was determined utilizing Tauc's equation. It is discovered that the band gap diminishes as the substrate temperature increments and the optical permitted energy gap for the direct electronic transitions was in the range of (2-2.2) eV. The optical absorption coefficient is found to be larger than (10^4 cm^{-1}), which respectively these films have a direct transition.

Keywords: *CZTS thin Films, Spray pyrolysis Technique, Optical properties, Energy gap.*

Introduction

Recently, the quaternary semiconductor Cu_2ZnSnS_4 has received considerable as attention one of the promising absorbers for the fabrication for thin film of solar cells with conversion efficiency close to 9.6%, which is the highest conversion efficiency of CZTS up to now[1]. CZTS compound was derived by replacing the first part of indium atoms, which is expensive element, with zinc and the other part with tin in the chalcopyrite-type lattice of $CuInS_2$[2].It has excellent physical properties, such as the direct band gap (~1.5 eV), high optical absorption coefficient > $10^4 cm^{-1}$, low thermal conductivity[3]. As well as the earth abundant and nontoxic constituent elements [4].It is derived from the CIGS structure by the isoelectronic Sn atom. As a consequence, CZTS has some similar properties as CIGS. The availability of Cu, Zn, Sn and S in the earth's crust are ~ 50, 75, 2.2 and 260 ppm respectively and the vailability of In is only ~ 0.049 ppm, so that all the constituents of CZTS are abundant in the earth's crust. Intrinsic point defects in CZTS make its conductivity p-type. Crystal structure of CZTS can allow some deviation from stoichiometry making its deposition process easier[5].Chemical spray pyrolysis (CSP) is an important preparation method for CZTS thin films because of its simplicity, moderate temperature processing and ability to prepare highly crystalline, large area thin films. In CSP method stoichiometry of CZTS is very sensitive to the concentrations of precursors in the spraying solutions[6].

Experimental

Thin films of Cu_2ZnSnS_4 were deposited on glass substrate by chemical splash spray pyrolysis method . Thin films of CZTS obtained using a simple home-built spray pyrolysis deposition. The antecedent arrangement was gotten by blending aqueous solutions of (0.01 mol/L) of CuCl,(0.005 mol/L) of Zn (CH3COO).$_2H_2O$, (0.005 mol/L) of ($SnCl_4$) and (0.04 mol/L) of $SC(NH_2)_2$ with a last volume of (100 mL) using deionized water. Using a hot plate, the substrate heated to the deposition temperature. The deposition parameters such as the Spraying distance (30 cm) from the nozzle to the substrate, spray angle (90°), spray time (5 s) and number of spray interval (20 min) were kept constant for all depositions. The carrier gas (filtered compressed air) flow rate was maintained at (6 L/min) at a pressure of (6.5×10^4 Nm) .But, the temperature of the substrate was variable (350,400 and 450) °C. The films were investigated by studying their composition, optical properties Absorption, Transmission, Absorption Coefficient (α), Optical Energy Gap Eg, Optical constant included Refractive Index (n), Extinction Coefficient (k) and Dielectric Constant (ε_r, ε_i) by using the UV-Vis spectroscopy.

Results and Discussion

Absorbance Spectrum

Optical transmission and absorption spectra depend on the chemical composition, crystal structure, energy of the incident photon, thin film thickness and thin film surface morphology [7]. Figur (1) Shows the absorbance decreases with increased wavelength of thin films.

Physically this means that the falling photon could not evaporate the electron and move it from the valence pack to the conduction beam because the falling photon energy is less than the energy value of the semiconductor and thus the absorbance is reduced by increasing the wavelength. Note also that the substrate temperature increases absorption due to decreased permeability due to increased particle size and roughness of the surface. Therefore, the thin films at substrate temperature (450) °C .Shows the highest absorption value in agreement with other reports [8, 9].

Transmittance Spectrum

Figure (2) shows the transmittance spectrum as a function of the wavelength of Cu_2ZnSnS_4 thin films in the region of (300-900) nm at (350,400 and 450)°C respectively. The films have high straight forwardness in the visible and near IR districts of the electromagnetic range with transmittance estimation of about (80 %).

It can be noticed that the transmittance for all thin films increments quickly as the wavelength increments, then increases slowly at higher wavelengths. It also shows that the optical transmittance decreases gradually as the substrate temperature expands which is in concurrence with different examinations [10,11].This is may be attributed to increasing the surface roughness. Therefore, the scattering light increases and the crystalline levels changes all thin films.

Reflectance Spectrum

The reflectivity is defined as the ratio between the intensity of the reflected beam and the intensity of the falling beam. The reflectivity is calculated using the spectrum of transmittance (T) and the absorption spectrum (A) under the energy conservation law. We observe from Figure (3) that there is an increase in reflectivity of all thin films with increasing wavelength and short duration followed by a rapid decline.

These peaks' are pushed towards the high photonic energies, indicating an increase in the energy gap by increasing the substrate temperature. It is also observed that the increase in deflection rates causes low reflectivity values. The ripples in reflectance spectra in CZTS thin films can attribute to optical interference effects [12].

Absorption Coefficient

Figure (4) demonstrates the optical absorption coefficient (α) as a function the wavelength of Cu_2ZnSnS_4 thin films. The values of (α) for all thin films are found to be greater than 104 cm-1 in the visible region, which means that the thin films have a direct optical energy gap [13].It depends on the energy of the falling photons and the properties of the semiconductor, which include the optical energy gap and the type of electronic transitions that occur between the region.

Therefore, we can determine the value of the optical energy gap by measuring the optical absorption coefficient. The value of the absorption coefficient at a rapid increase, in which we can deduct the absorption edge. Not that the absorption edge is not sharp but on the shape of a curve and this indicates that thin films prepared in this way are polycrystalline

Energy Gap

Optical band gap Eg of the samples was deduced from the plot of $(\alpha h\mathbf{v})^2$ vs. h**v**, by extrapolating the straight line portion of the graph in the high absorption regime (Figure 5). The $(\alpha h\mathbf{v})^2$ versus h**v** plots for thin films deposited at substrate temperature equal to (350, 400, and 450 °C) are shown in (Figure

5). The direct optical band gaps are found to be of about (2, 2.1, and 2.23 e v), respectively. So, the band gap energy Eg of the thin film deposited at (450°C) is quite close to the optimum value for solar cells [14]. Reported that the CZTS film prepared using $SnCl_2$ exhibited a direct band gap of about (1.3 eV). The presence of ZnS phase causes the enlargement of the optical band gap since this phase has a large band gap of (3.5 eV). Optical broadening which is due to the incorporation of ZnS as secondary phase in $CuInS_2$ was also observed Deranged et al [15].

Reported also that a fraction of $ZnSnO_3$ phase in CZTS causes the enlargement of the optical band gap. In the recent research [16]. It is demonstrated that the existence of ZnSe within CZTSe films is the presumable reason for the rise of Eg from 1 to (1.5 eV). Another small peak of ZnS may be due to the increase of the peaks intensities of CZTS. It very well may be seen that the band gap esteem diminishes as the substrate temperature builds, which is in concurrence with report [17].

Extinction Coefficient

Excitation coefficient is calculated by using equation :

$n_c = n - {}_i k$...(1)

Figure (6) shows the variation of (k) as a function of wavelength for all (Cu_2ZnSnS_4) prepared thin films, we can observe that there is a small increase to extinction coefficient values at low photon energies values then follows a sample increase in the high energies near the energy gap, this increase in the coefficient of extinction due to the increase in the value of the absorption coefficient and this increase indicates the occurrence of electronic transitions between the valence and conduction band. Which led to increase absorption coefficient this can be attributed to the increase in the formed accepter levels within energy gap [18].

Refractive Index

The refractive index (n) is an important parameter for optical materials and applications. Figure (7) show the variation in refractive index of thin films with wavelength. The refractive index decreases gradually with increasing of wavelength. It tends to be seen that the refractive list has an expanding pattern with substrate temperature for explanation of this behavior may be related to the polarization of thin film because the refractive index value (n) depends on material polarization where with increasing of polarization the velocity of light was decreased so refractive index changed. The polarization depends on the crystalline and on the grain size of thin film so these depend on preparation conditions [19].

Dielectric Constant

Both real (ε_r) and imaginary (ε_i) dielectric constant are measured for prepared films by usin g relationships:

$$\varepsilon_r = n^2 - k^2 \quad \cdots\cdots\cdots (2)$$

$$\varepsilon_i = 2\,n\,k \quad \cdots\cdots\cdots (3)$$

Figures (8) and (9) illustrate variation of (ε_r) and (ε_i) as a function of wavelength. It is observed that their values increase with increasing of wavelength and real dielectric constant behave like refractive index we can see increases in the high energies near the energy gap accompanying change in substrate temperature which means that the real dielectric constant increase with increasing of substrate temperature. It is seen that the value of real part is higher than the imaginary part. from the above not that the increase in the proportion of thin film lead to rearrange the localized state causing an decrease in conductivity film on the account increases in fixed real isolation [20].

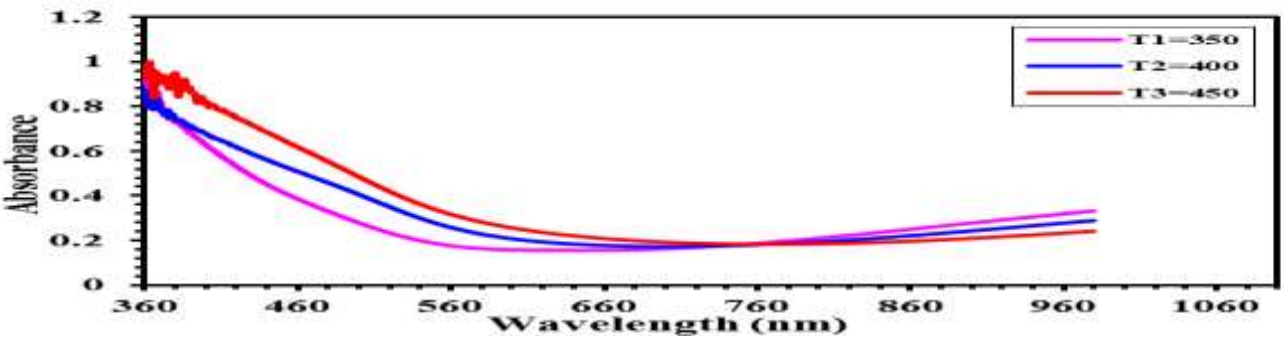

Figure 1: Absorbance spectrum for (Cu_2ZnSnS_4) thin films at different substrate temperature

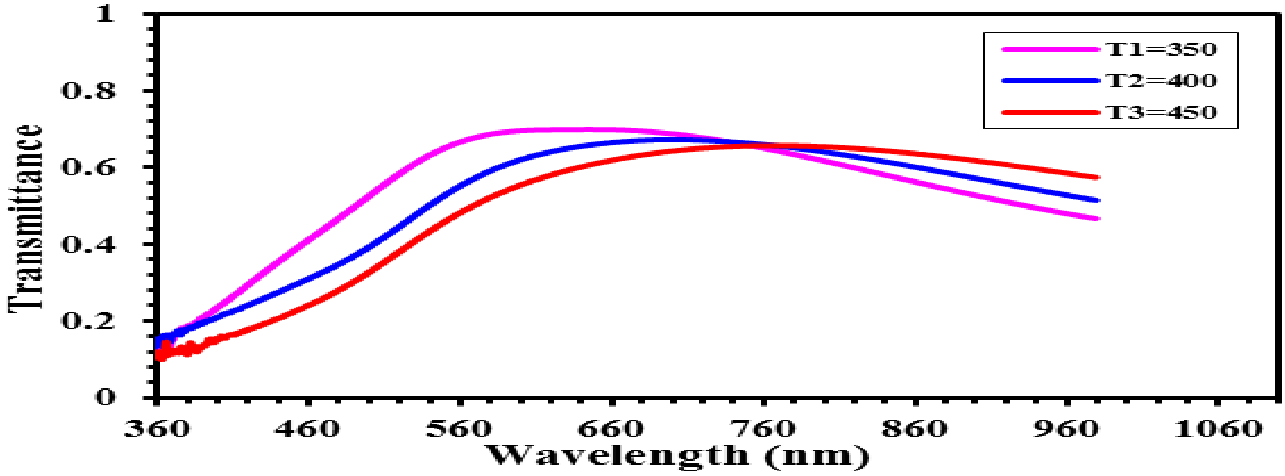

Figure 2: Transmittance spectrum for (Cu_2ZnSnS_4) thin films at different substrate temperature

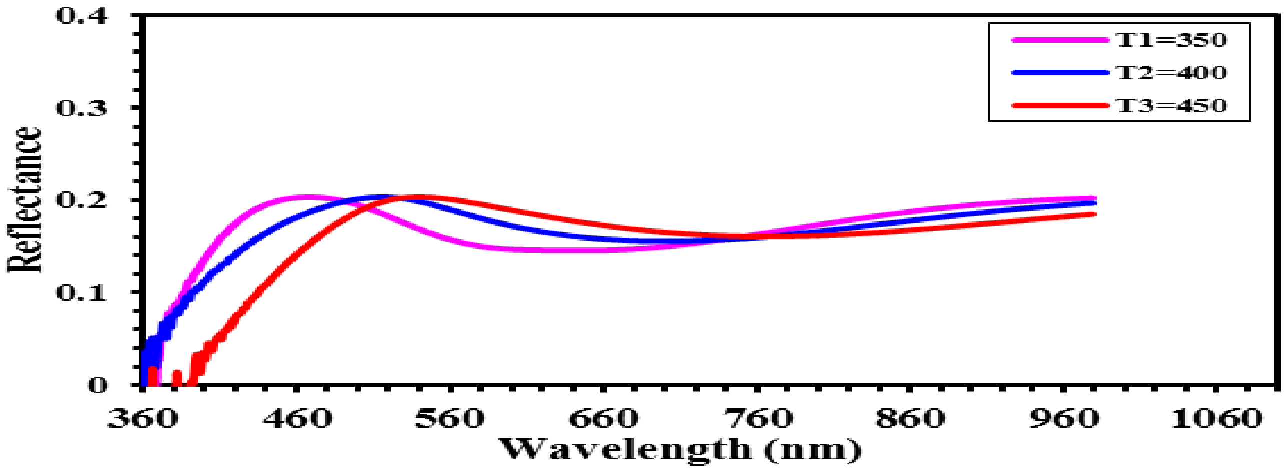

Figure 3: Reflectance spectrum for (Cu_2ZnSnS_4) thin films at different substrate temperature

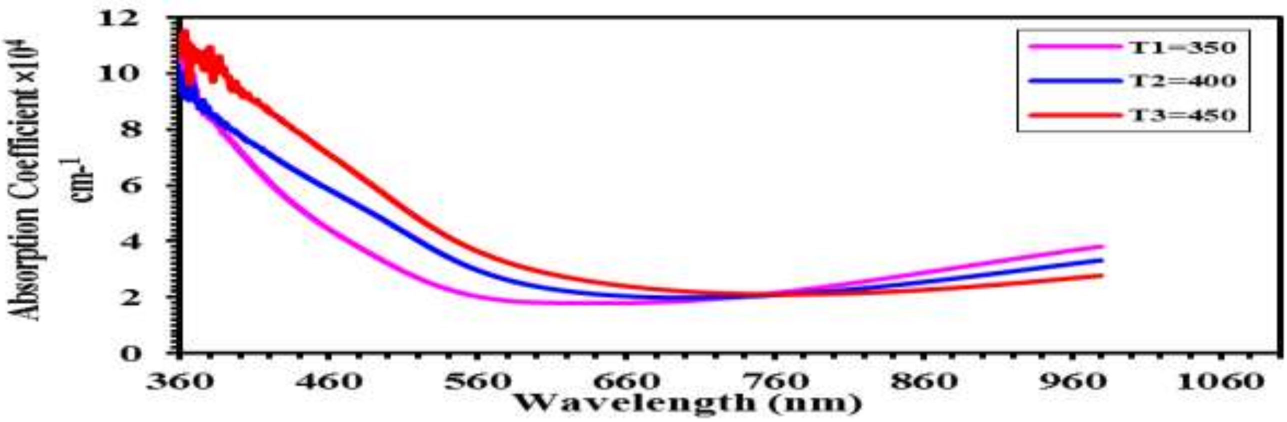

Figure 4: Absorption coefficients for (Cu_2ZnSnS_4) thin films at different substrate temperature

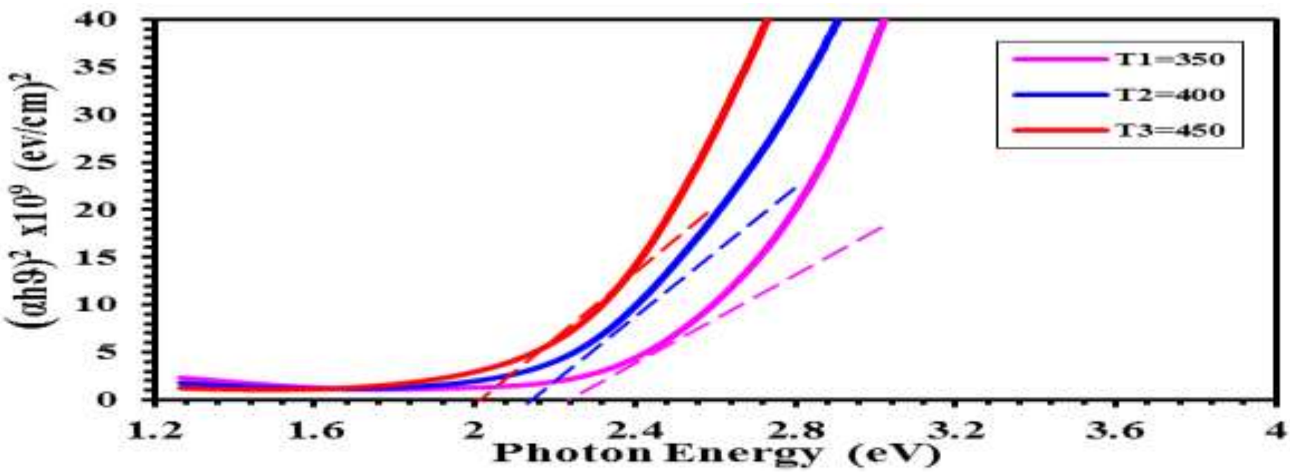

Figure5 :$(\alpha\ h\nu)^2$ as a function of photon energy for (Cu_2ZnSnS_4) thin films at different substrate temperature

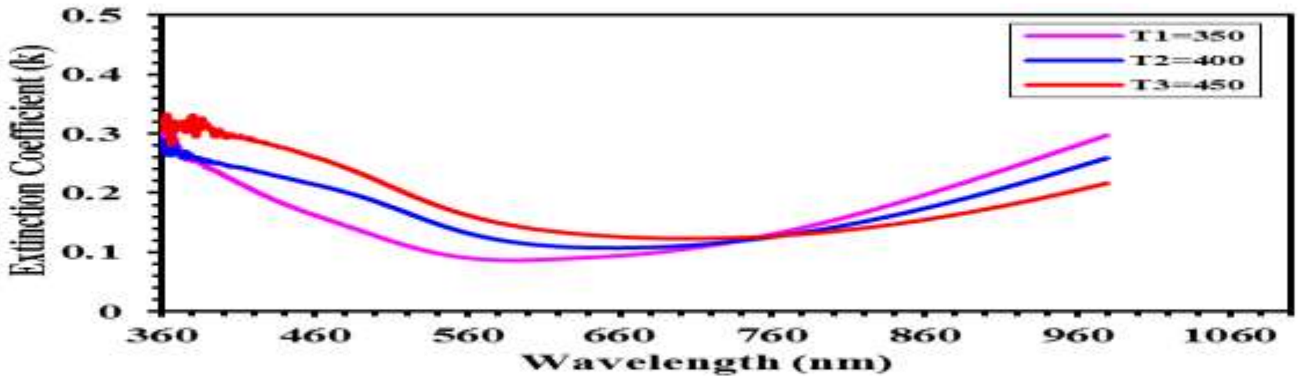

Figure 6: Extinction coefficient for (Cu_2ZnSnS_4) thin films at different substrate temperature

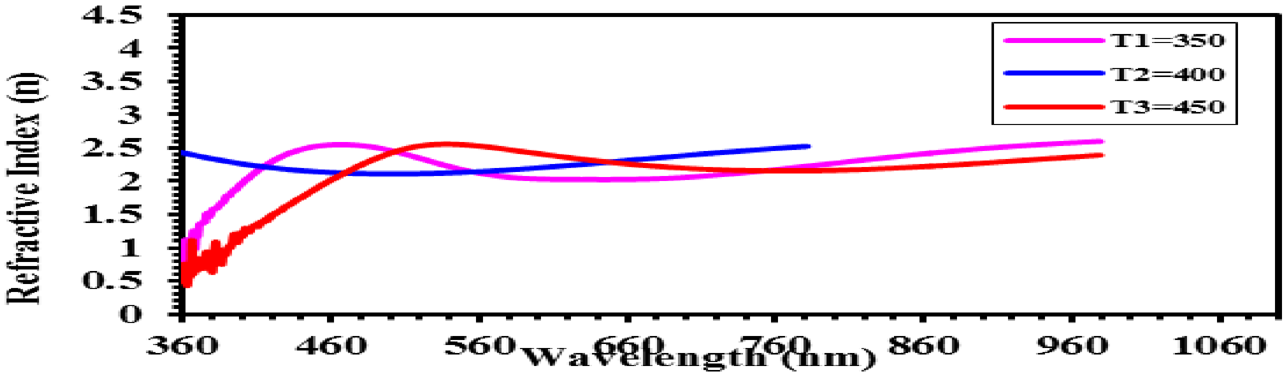

Figure 7: Refractive Index versus wavelength of (CZTS) thin films at different substrate temperature

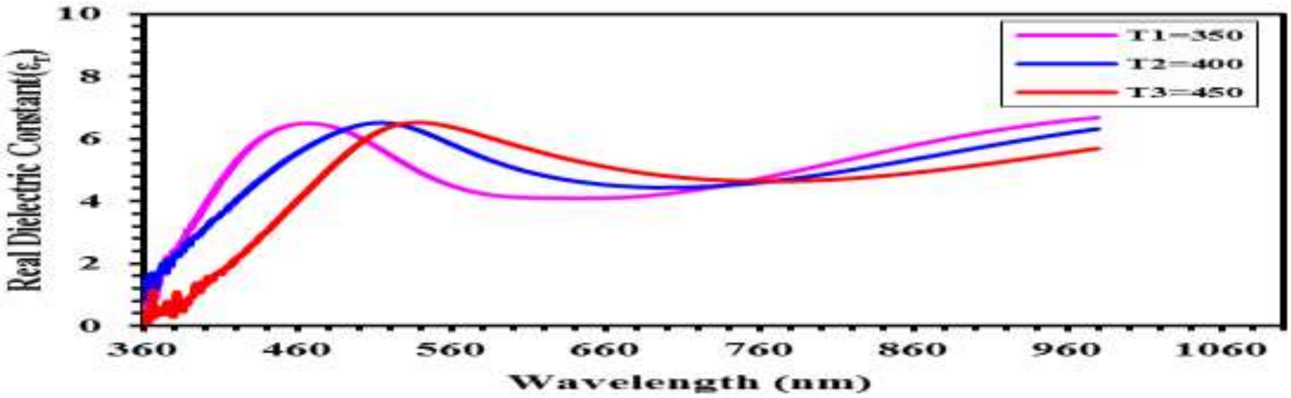

Figure 8: Real dielectric constant for (Cu_2ZnSnS_4) thin films at different substrate temperature

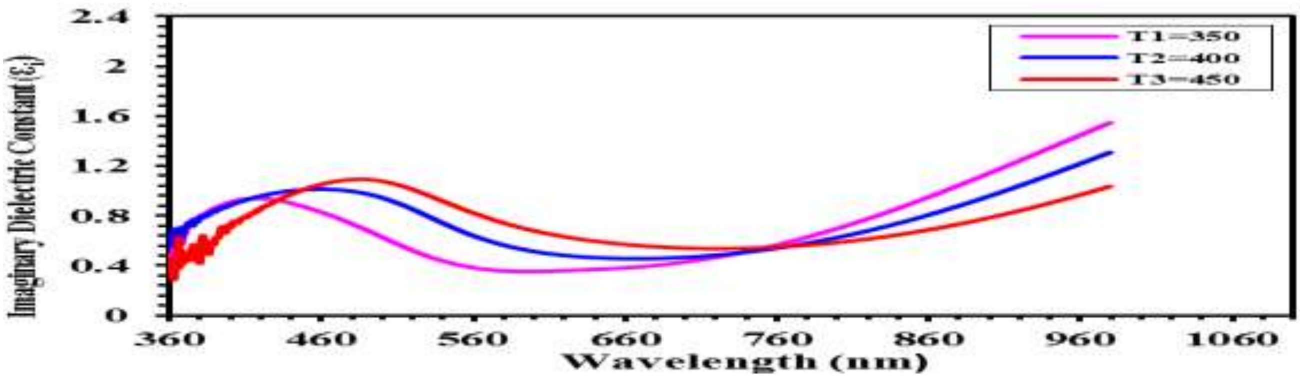

Figure9: Imaginary dielectric constant for (Cu_2ZnSnS_4) thin films at different substrate temperature

Conclusions

The optical properties of (Cu_2ZnSnS_4) thin films have been determined by using the optical transmittance measurements in the spectral region from (300 to 1000 nm).Transmittance results were upper than 80% which make these thin films suitable for sensor applications. Direct energy gap for highest temperature(T=450 °C) equal 2 eV, has the best crystalline, the lowest resistivity, the optical constants such as refractive index, extinction coefficient and dielectric constant have been calculated for all preparing thin films.

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