

The Optical Properties of AgAlSe₂ Thin Films Doped In

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ABSTRACT: In this work, the AgAlSe₂ doped In has been studied by using the thermal vacuum evaporation method on glass substrate at room temperature with the chemical formula (AgAl_{1-x}In_xSe₂) where x=0.3,0.6,0.9. The optical properties of the prepared films have been investigated. The optical absorption coefficient (α) of the films was determined from absorbance spectra in the range of wavelength (400-1100) nm. The optical energy gap was found allowed direct transition, which decreases as the In-content (x) change from x=(0.3-0.9).

KEYWORDS: Ag (Al, In) Se₂, thin films, thermal evaporation, energy gap, optical properties.

I. INTRODUCTION

Chalcopyrite semiconductors are used as the absorber layer which is the most important layer in the PV device, reducing the thickness of absorber layer is the another approach to reducing the overall cost of the solar cell, decreasing the thickness of a thin layer below 1 micron could lead to a reduction in the production cost, with no, or only minor, loss in performance [1]. The ternary ABC₂ chalcopyrites (A = Cu,Ag; B = In, Ga or Al; C= S, Se or Te) form a large group of semiconductor materials with diverse structural and electrical properties. These materials are attractive for thin film photovoltaic application for a number of reasons [2]. Cu based chalcopyrites are most intensively studied, but few experimental and theoretical studies of ABC₂ type semiconductors where group A element is Ag and the group B element is Al have been carried out [3].

Ag chalcopyrites has several advantages over Cu chalcopyrites such as:

The band gap energy of Ag chalcopyrites films is wider than Cu chalcopyrites [4] and the melting point of the Ag chalcopyrites film is lower than Cu chalcopyrites which make them commercially more preferable [5]. The band gap of AgAlSe₂ is relatively high, 2.5 eV, but it can be used to better match the solar spectrum either by substituting part of Al by In, Ga or part of Se, Te by S. The flexibility of the material system allows in principle the band gap variation from 1.00 eV of AgInTe₂ to 3.13 eV of AgAlS₂ [6,7].

Most of the I-III-VI₂ compounds are direct gap semiconductors and they crystallize with the chalcopyrite structure [8].

II. EXPERIMENTAL

Thin films AgAl_{1-x}In_xSe₂ (AAIS) with x=0.3,0.6,0.9. Have being deposited on a glass substrate by a thermal vacuum evaporation method using (Edwards – Unit 306) system with 4.5x10⁻⁵ mbar at room temperature. The thickness of films was determined by (Precisa-Swiss) microbalance using weighing methods and it was about (500±10) nm, with a deposition rate about (5±0.1) nm/Sec. Molybdenum boat with cover include pin holes was used for films preparation with distance about (15)cm from the substrate. A spectrophotometer model (UV-Visible 2601) double-beam spectrophotometer is used to measure the transmittance and the absorbance spectrum in the range (400-1100) NM region for all Ag (Al, In) Se₂ thin films. The ability of a material to absorb light is measured by its absorption coefficient and it is a very strong role of the photon energy and band gap energy [9].

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The optical absorption spectrum is used to determine the optical energy gap and the absorption coefficient. Knowledge of these band gaps is extremely important for understanding the electrical properties of a semiconductor, and is therefore of great practical interest [10].

The fundamental absorption, which corresponds to electron excitation from the valance to the conduction band, can be used to determine the character and value of the optical band gap. The optical band gap of the films is calculated using the expression [11]:

$$\alpha h\nu = B (h\nu - E_g^{opt})^{1/r} \dots\dots\dots(1)$$

where, B is a constant depending on the type of semiconductor, $h\nu$ is the photon energy (eV), E_g^{opt} is the optical energy gap (eV), and r is constant and may take values 2, 3, 1/2, 3/2 depending on the material and the type of the optical transition. There are two types of the optical transitions, direct and indirect transition, according to the type of materials and optical transition.

The absorption coefficient values can be calculated from the formula [9]:

$$\alpha = 2.303 \frac{A}{t} \dots\dots\dots(2)$$

where A is the optical absorbance and t the film thickness.

When electromagnetic rays strikes a surface, some part is reflected, some is absorbed and some is transmitted. The optical constants fully express the optical behavior of materials; they are important fundamental properties of matter [12,13]. Optical constants included refractive index (n), extinction coefficient (k), real part (ϵ_r) and imaginary parts (ϵ_i) of dielectric constant. The refractive index (n) can be calculated using following equation[14]:

$$n_o = \left[\frac{4R}{(1-R)^2} - k^2 \right]^{\frac{1}{2}} + \left(\frac{1+R}{1-R} \right) \dots\dots\dots(3)$$

where R is the reflectance. which is calculated by the relation[14]:

$$R=1-A-T \dots\dots\dots(4)$$

The Extinction coefficient, k (imaginary part of the refractive index), which is related With the exponential decay of the wave as it passes through the medium can be determined by using the equation [15]

$$k = \frac{\alpha \lambda}{4\pi} \dots\dots\dots(5)$$

Where, λ : is the wavelength of the incident radiation.

The real ϵ_r and imaginary ϵ_i part of dielectric constant are related to the n and k values and can be calculated by using the following equations[16]:

$$\epsilon = \epsilon_r - i\epsilon_i \dots\dots\dots(6)$$

$$\epsilon_r = n_0^2 - k_0^2 \dots\dots\dots(7)$$

$$\epsilon_i = 2n_0k_0 \dots\dots\dots(8)$$

III. RESULT AND DISCUSSION:

The experimental absorption spectra for the $AgAl_{1-x}In_xSe_2$ for x=0. 3,0.6,0.9. thin films were made at room temperature in the spectral range (400-1100) nm are shown in Figure (1). All spectra show better absorption in the visible regions. The optical absorption increases as a function of In content. When the x increases the absorption increases and close for visible region. The absorption is maximum for x = 0.9 and reaches a value of 88.9% at 490 nm of photon wavelength. The behavior of the absorption spectra is opposite completely to that of the transmission and reflection spectra, as shown in Figures (2 and 3).

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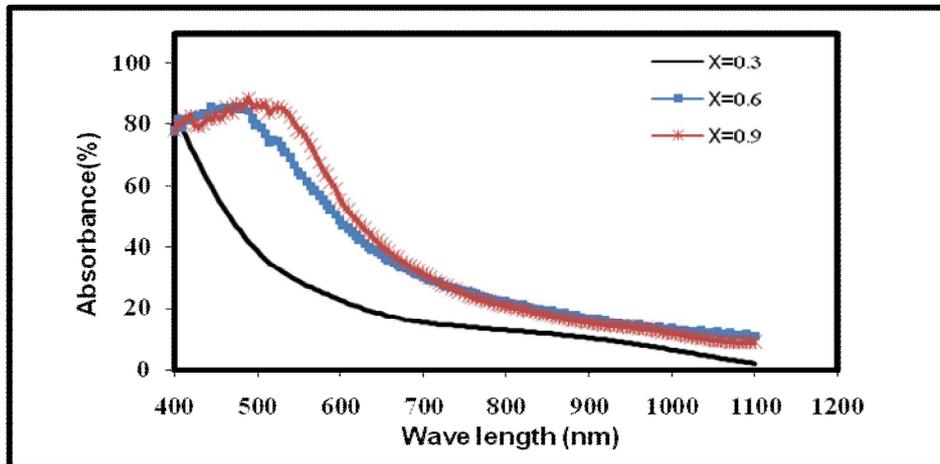


Figure (1): Absorbance spectra for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

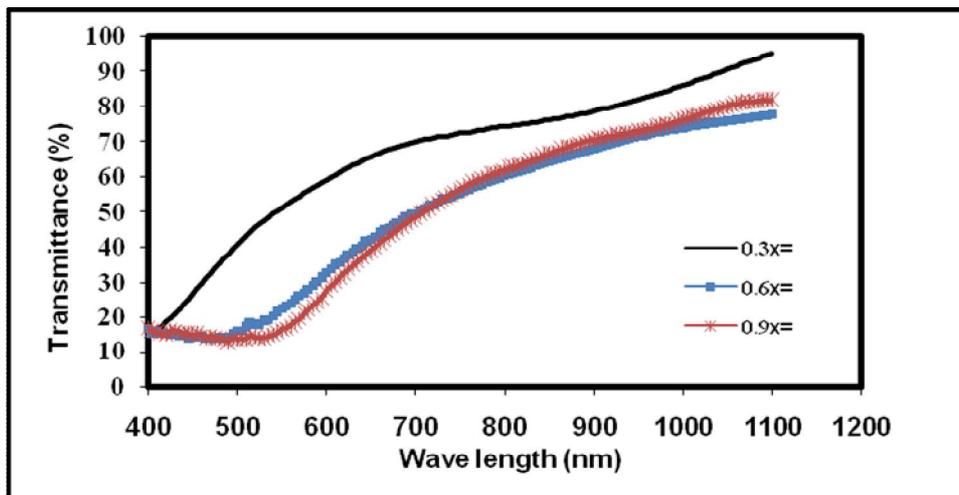


Figure (2): Transmittance spectra for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

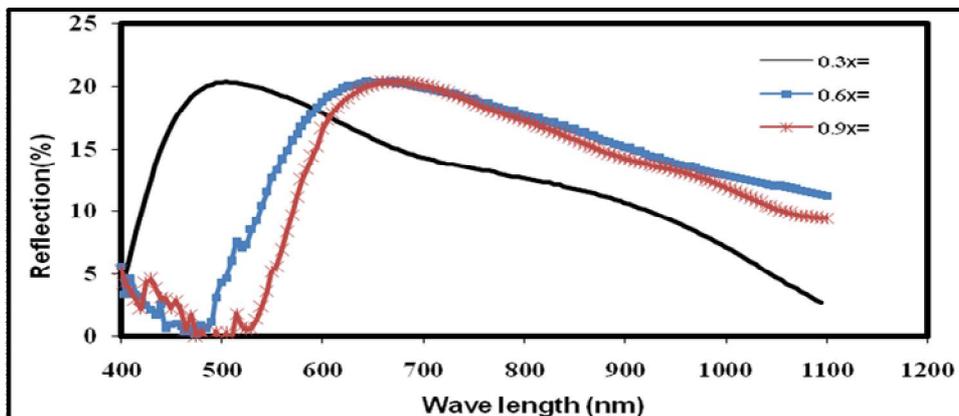


Figure (3): Reflectance spectra for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

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From Figure (4) it is observed that the absorption coefficient (α) values, which were calculated using equation (2). The absorption coefficient α exhibits high value reached above 10^4 cm^{-1} , which means that there is a large probability of the allowed direct transition, and then α decreases with increase of wavelength and the coefficient absorption values increase with the decrease of optical energy gap. This variation could be related to the variation of the crystallinity and carrier concentration of $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$.

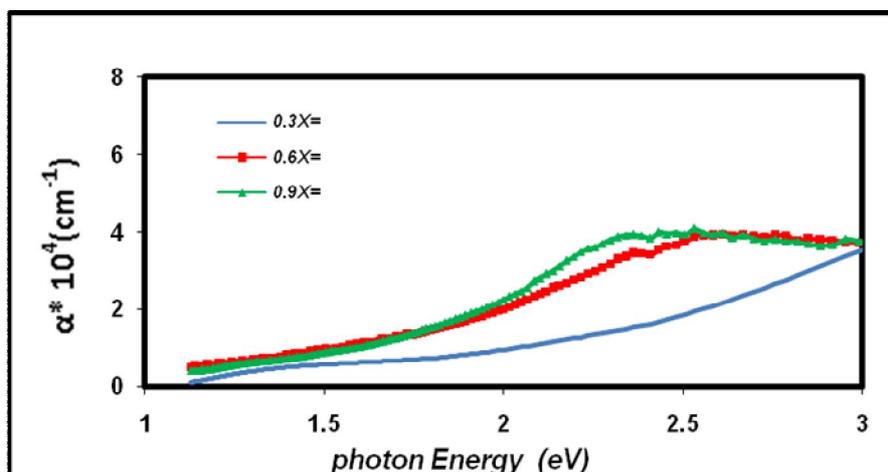


Figure (4): Variation of absorption coefficient with photon energy for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

The optical energy gap of material can be determined using the equation (1), by plotting of $(\alpha h\nu)^2$ versus $h\nu$ for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films with $x=0.3,0.6,0.9$ was shown in Figure (5). The curve is linear at the absorption edge which confirms that the $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ semiconductor film have direct band gap. Extrapolation of the line to the $h\nu$ axis determines the optical band gap its types were allowed direct.

It can be noticed from the values of E_g^{opt} that it decreases with the increase in the value of x as shown in Figure (6) and table (1) This behavior agrees with that shown by other researcher [17]. This is due to an increase in practical size [18][19], the decrease of direct band gap with the increase of In content can be attributed to the increase of particle size, decrease of the strain and increase of lattice constant [20].

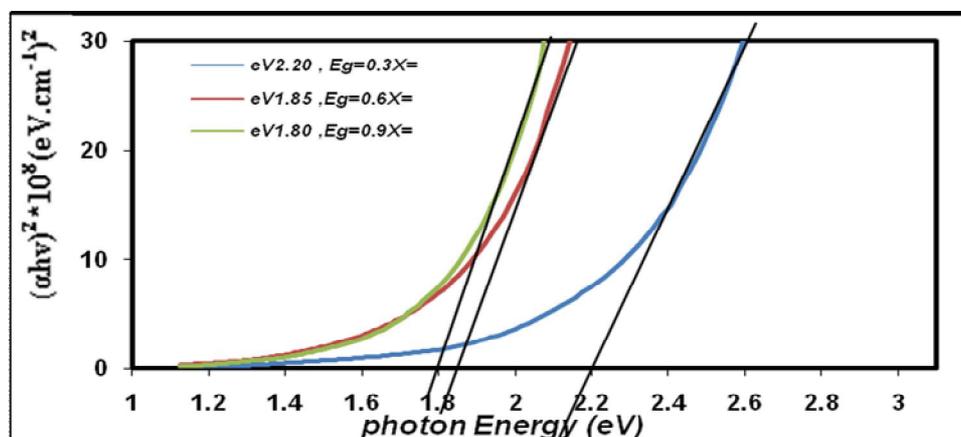


Figure No.(5): Variation of $(\alpha h\nu)^2$ with photon energy for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

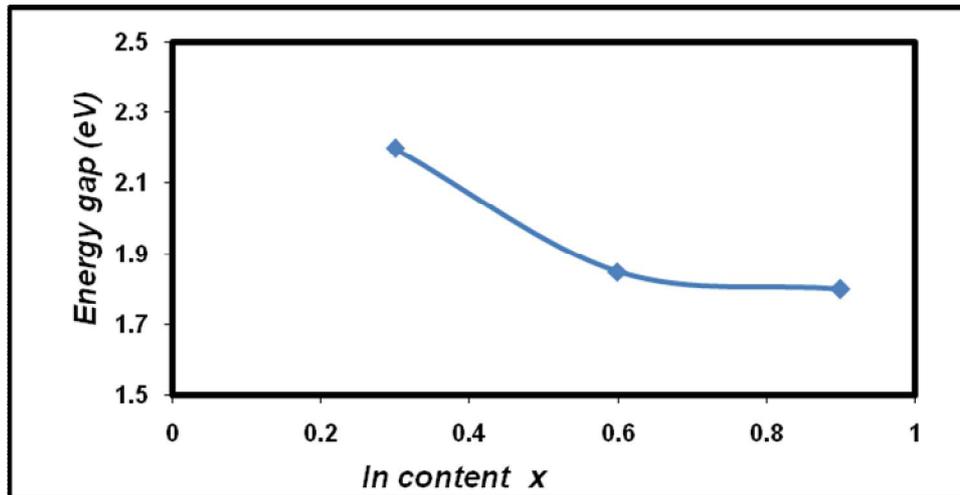


Figure No.(6): Variation of energy gap of $AgAl_{1-x}In_xSe_2$ as a function of In content.

The refractive index dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion. The refractive index values of the films were calculated using Eq (3). The behavior of refractive index is nearly similar to the reflectance spectra. Dependence of refractive index of photon energy of $AgAl_{1-x}In_xSe_2$ thin films with different In concentrations has been shown in figure (7). Refractive index increases with the increase of photon energy for $AgAl_{1-x}In_xSe_2$ films at different values of x as shown in figure (7). It is clear that the refractive index increases with the increase of photon energy followed by decreases at the higher photon energy.

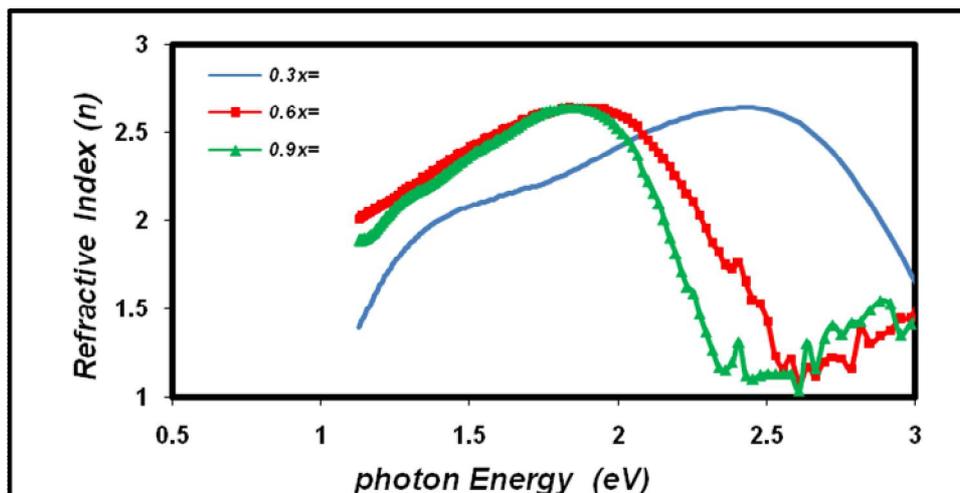


Figure (7): Variation of refractive index with photon energy for $AgAl_{1-x}In_xSe_2$ thin films for $x=0.3,0.6,0.9$.

Fig. 8 shows the variation of extinction coefficient (k) as a function of photon energy. The behavior of (k) is nearly similar to the corresponding absorption coefficient (α) because of the extinction coefficient depends mainly on (α) values according to the Eq (5); for this reason, we notice the increase of extinction coefficient as a function of photon energy due to the increase of the absorption coefficient. This means that direct electronic transition happens in these films [21].

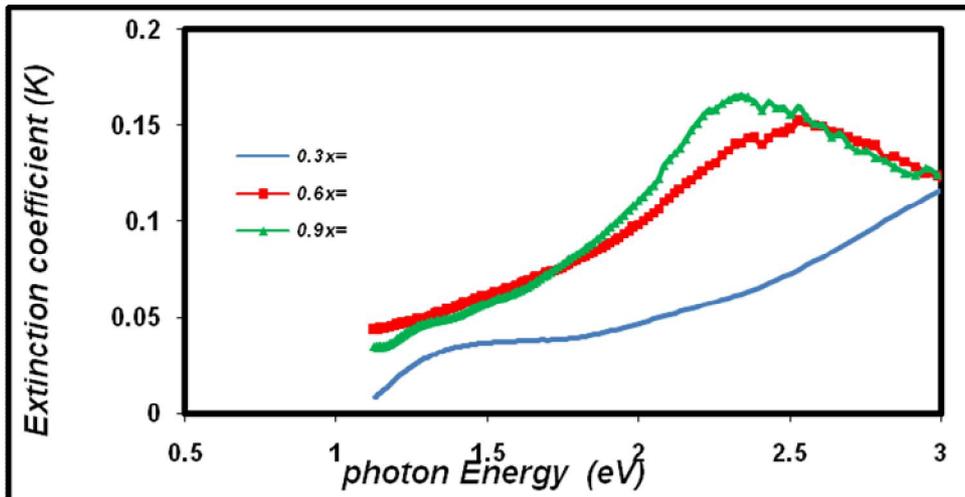


Figure (8): Variation of Extinction coefficient with photon energy for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

The dielectric constant consists of a real (ϵ_r) and imaginary part (ϵ_i) depends on the frequency of the electromagnetic wave. The variables of ϵ_r and ϵ_i versus photon energy at different values of x are shown in Figures (9 and 10) respectively. The behavior of ϵ_r is similar to that of the refractive index because of the small value of k^2 compared with n^2 , while ϵ_i behavior is similar to that of extinction coefficient because it mainly depends on the k value, which is related to the variation of absorption coefficient. All the films show same trend.

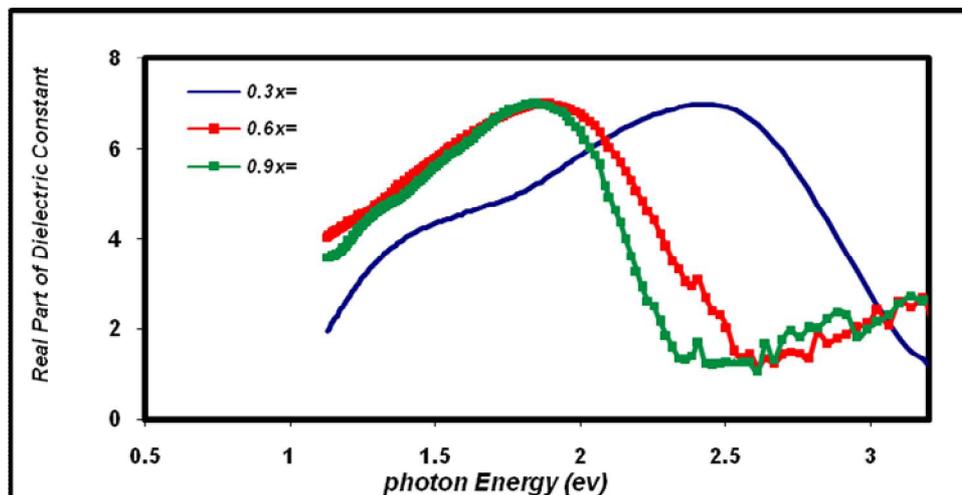


Figure (9) Variation of *real part of dielectric constant* with photon energy for $\text{AgAl}_{1-x}\text{In}_x\text{Se}_2$ thin films for $x=0.3,0.6,0.9$.

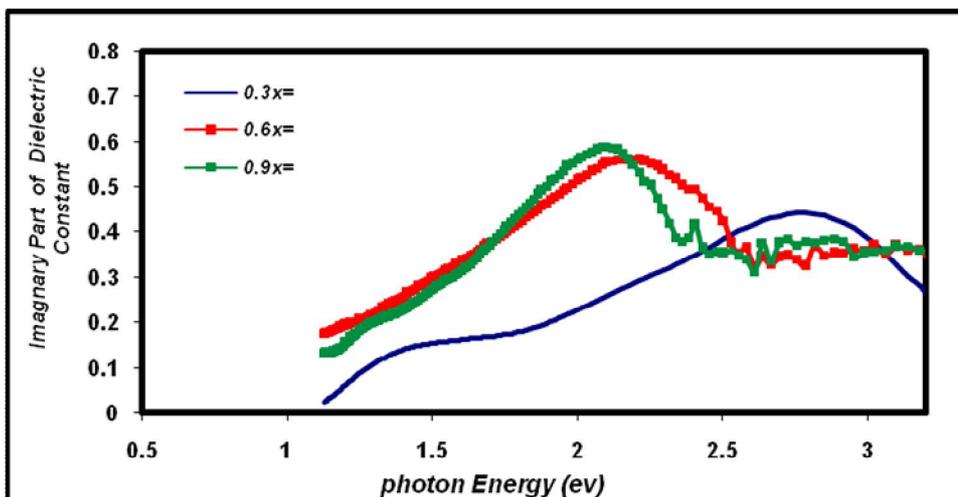


Figure (10) Variation of of imaginary part of dielectric constant with photon energy for AgAl_{1-x}In_xSe₂ thin films for x=0.3,0.6,0.9.

Table (1): The optical parameters (E_g^{opt} , α , k, n, ϵ_r and ϵ_i) for Ag(Al,In)Se₂ thin films for x=0.3,0.6,0.9 at $\lambda=490$ nm.

$\lambda=490$ nm						
X	E_g^{opt} (eV)	$\alpha \times 10^4$ (cm) ⁻¹	n	k	ϵ_r	ϵ_i
0.3	2.2	1.92	2.618	0.075	6.84	0.39
0.6	1.85	3.899	1.23	0.152	1.5	0.37
0.9	1.8	4.09	1.13	0.159	1.25	0.36

IV. CONCLUSIONS

The AgAl_{1-x}In_xSe₂ films were deposited by physical vapor deposition in vacuum technique. The optical properties of the AgAl_{1-x}In_xSe₂ films were influenced with the In concentrations at room temperature. It was observed that absorbance in the visible region is high. Absorption coefficient had been calculated from absorption spectra taken within the wavelength of (400 to 1100) nm. The calculated absorption coefficient was found of the order of 10⁴ cm⁻¹ in the higher energy region and the rate of absorption is max near the absorption edge, which is around 490 nm. The optical band gap values were found to decrease from 2.2 to 1.8 eV as the In concentrations from x=0.3 to 0.9. The optical constants of the films had been investigated in this work, and they depend on the In concentrations, finally it may be concluded that the AgAl_{1-x}In_xSe₂ films suitable for optoelectronic devices, for instance as window layers of solar cells.

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