Comparing the optical parameters for thin CAZTSe films prepared with various Ag ratios and annealing temperatures

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Hanaa I. Mohammed, Iman H. Khdayer and Iqbal S. Naji

Comparing the Optical Parameters for Thin CAZTSe Films Prepared with Various Ag Ratios and Annealing Temperatures

Hanaa I. Mohammed[a], Iman H. Khdayer, Iqbal S. Naji

Physics Department, University of Baghdad, Iraq

[a]Corresponding author: hannaibraheem687@gmail.com

Abstract. Pure Cu (CZTSe) and Ag dopant CZTSe (CAZTSe) thin films with Ag content of 0.1 and 0.2 were fabricated on coring glass substrate at R.T with thickness of 800nm by thermal evaporation method. Comparison between the optical characteristics of pure Cu and Ag alloying thin films was done by measuring and analyzing the absorbance and transmittance spectra in the range of (400-1100)nm. Also, the effect of annealing temperature at 373K and 473K on these characteristics was studied. The results indicated that all films had high absorbance and low transmittance in visible region, and the direct bang gap of films decreases with increasing Ag content and annealing temperature. Optical parameters like extinction coefficient, refractive index, and dielectric constants were estimated.

Keywords: CAZTSe alloy and thin films, optical parameters, thermal evaporation method

INTRODUCTION

Multicomponent chalcogenide semiconductors have attracted a wide attention for their various uses such as thermoelectricity, photocatalysis, and photovoltaics(1, 2). The quaternary compound $Cu_2ZnSnSe_4$ is considered to be one of these semiconductors(3). It received a lot of care in the last years as a substitute absorber material for thin film solar cell because of its intrinsic high absorption coefficient ($\alpha > 10^4 cm^{-1}$), contain only earth- abundance , nontoxic elements(4, 5), and has a direct band gap of 1.5eV(6), which is ideal for solar cell applications. Lately, CZTSe semiconductor compound showed better photoconversion efficiency (PCE) than PCE for Cu_2SnS_3 and Cu_2ZnSnS_4 semiconductor compounds(7,8), but it remains less than PCE for commercial solar cell, because of its open circuit potential (V_{oc}) limitation(9). So, essential treads are required to develop the PCE of thin CZTSe films to reach commercial aim. By changing the thin CZTSe films electrical and optical characteristics their PCE can be tuned(10). Thin CZTSe films electrical characteristics can be improved by suitable alteration in their elemental stoichiometry and/or doping(1). While thin CZTSe films optical characteristics can be tuned by alteration thin films parameters or preparation techniques(10). Although silver is considered as non-earth-abundant element(9), but Ag alloying is an important way to solve V_{oc} limitation in thin CZTSe films solar cells(11). Ag has ability to suppress antisite defects (Cu_{Zn}), which formed in high densities in thin CZTSe films which cause V_{oc} limitation(12), this is due to Ag returns to the same chemical group for Cu, and it has atomic radius nearly 16% larger than Cu(13). In 2012 Sasamura et al., have investigated that Ag- based quaternary semiconductor materials gave higher PCE than pure thin CZTSe films(14), while in 2016 Gershon et al., estimated that the carriers density of CAZTSe absorber layer decreases with increasing Ag ratio(13). Researchers are used various techniques to grown thin CZTSe films(15-18), which include vacuum and non-vacuum based techniques.

In this work thermal evaporation technique was adopted to prepare thin $(Ag_xCu_{1-x})_2ZnSnSe_4$ films from their prepared alloys and then the effect of Ag content and annealing temperature on their optical properties was investigated.

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MATERIALS AND METHODS

To prepare $(Cu_{1-x},Ag_x)_2ZnSnSe_4$ alloys with different Ag content where x =0.0,0.1,0.2, appropriate atomic percentages with high purity 99.999% of Cu, Ag, Zn, Sn, Se elements which obtained from Fluka company were taken by using sensitive electrical balance type (Mettler H35 AR). These elements were put in clean and dry quartz ampoules, and then the ampoules were linked by specific design to the vacuum unit. When the pressure reached 10^{-3} Torr, the ampoules were sealed off. The loaded capsules were first put in containers and placed inside an electrical a programmable furnace kind Carbolite. The furnace temperature was gradually raised with four steps to 1373 K which is above the melting point of Cu (1356.6K), Ag (1234.7K), Zn (692.5K), Sn (504.9K), and Se (494K) .Then the capsules were kept at this temperature for 7h. Finally these ampoules were quenched rapidly in cold water to reduce segregation and to obtain more homogenous alloys. After this capsules were broken to bring out the $(Cu,Ag)_2ZnSnSe_4$ alloys. These alloys powdered and kept in small ampoules. The powder of compounds was used as source of the evaporation to prepare the films.

Edwared Coating unit model 306A with pressure of 10^{-5} Torr was used as vacuum unit to prepare $(Cu,Ag)_2ZnSnSe_4$ thin films on a cleaned corning glass substrate at room temperature with thickness of 800 nm and deposition rate of 0.53nm/sec.

Absorbance and transmittance spectra in the range 400-1100 nm were recorded by utilizing a spectrometer of the type (UV-Visible 1800 Spectrophotometer), using a blank substrate as the reference position to study the effect of Ag content and temperature of heat treatment on the optical constants of all prepared thin films.

The optical absorption coefficient (α) was estimated by utilizing the following equation[19]:

$$\alpha = 2.303 -$$

Where A: film optical absorbance, and t: film thickness.

The refractive index (n) was calculated from equation below[20]:

Where k: the film extinction coefficient, and R: the film reflectance.

The extinction coefficient is correlated to α and wavelength (λ) as[21]:

The real and imaginary parts of dielectric constant can be estimated from the following equations[22]:

RESULTS AND DISCUSSION

Optical studies give good information about the properties of semiconductors, such as study the optical absorption coefficient for different energies gives details about materials band gap, which is very important for understanding semiconductor electrical properties, also its important for practical application[23].

Figure1(a) (b)(c) displays the absorbance spectra of as deposited and annealed at 373K and 473K in vacuum for one hour for pure Cu and Ag doped thin films grown on coring glass substrate at R.T with thickness of 800nm. It is obvious from Fig. 1a that as deposited films have a good absorbance in the visible part of spectrum and it improves clearly with reducing the wavelength until reach maximum at 400nm. This may be resulted from band to band absorption of incident photon[10, 24]. Furthermore, the films absorbance reduces to lowest magnitudes in IR region. This result agreement with Henry et. al.[10, 25] for pure Cu thin films. Another observation from the figures that the film absorbance increases with increasing Ag content, which is produced from the fact that Ag has ability to absorb visible light due to Surface Plasmon Resonance a silver-related phenomenon[26]. This phenomenon is generated when the electrons near the surface of metal interact resonantly with electromagnetic field of light[27]. By comparing Fig 1(a) with Fig 1 (b&c), one can be noticed that the film absorbance increases with increasing the temperature of annealing, and this can be resulted from development of film crystallinty with annealing temperature as estimated from XRD analysis in our earlier repot[28]. Consequently these films have low transmittance in the visible region and the film transmittance decreases with increasing Ag content and annealing temperature as shown in Fig (2a,b&c). This is because transmittance has completely opposite behavior to corresponding absorbance. So, these films are used as appropriate absorber material for solar cell application.

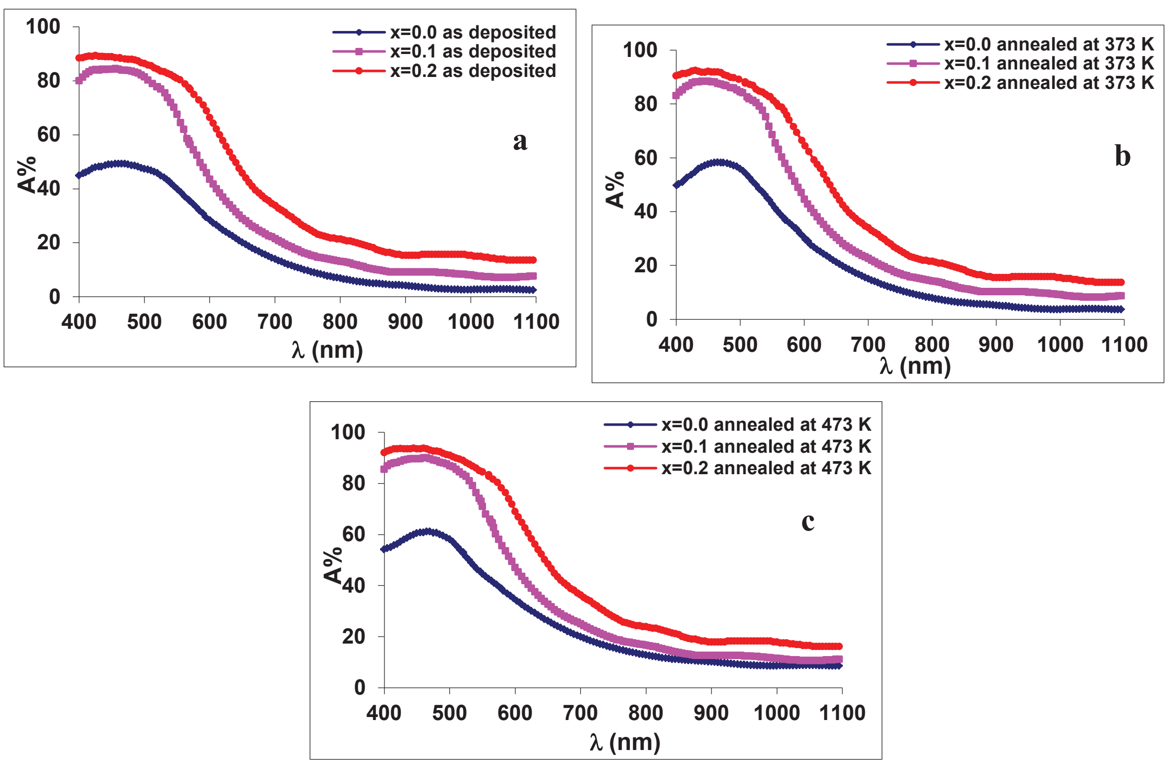

FIGURE 1. Absorbance as a function of wavelength for thin $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ films of different Ag ratios at: (a) R.T, (b) 373K, (c) 473K.

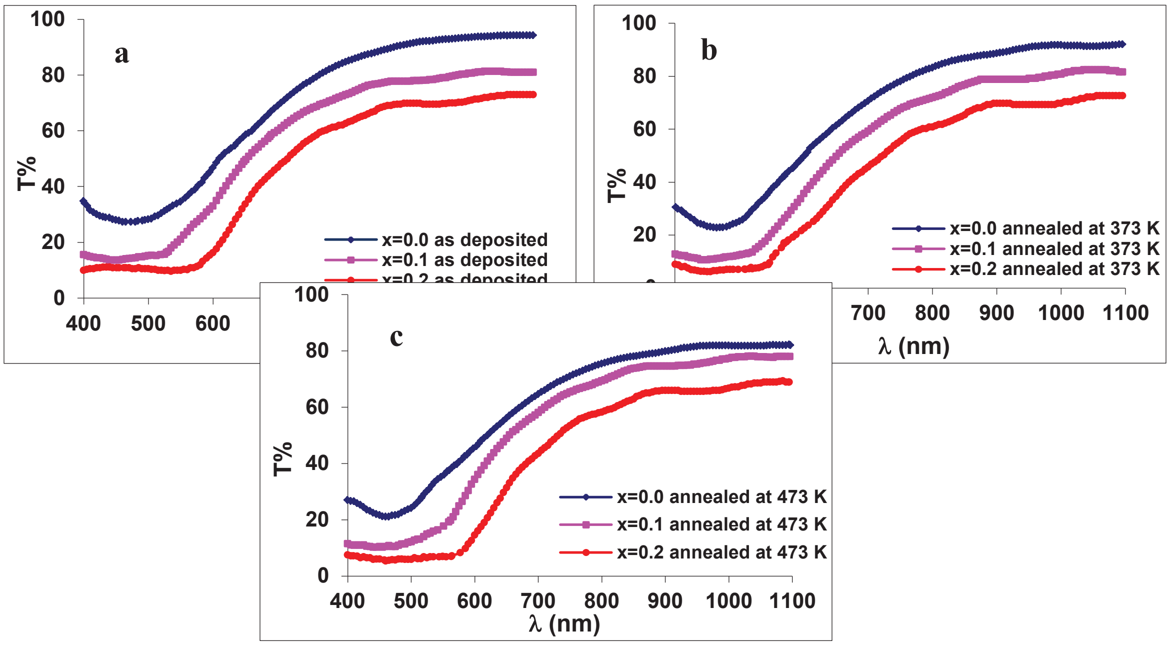

FIGURE 2. Transmittance as a function of wavelength for thin $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ films

of different Ag ratios at: (a) R.T, (b) 373K, (c) 473K.

The optical energy band gap (E) for as deposited and annealed at 373K and 473K thin CAZTSe films with various Ag content (0.0, 0.1, and 0.2) was estimated using Tauce relation [29]:

Where B: constant which including the properties of the bands, and r: constant depending on the transition nature. This equation is utilized to examine the kind of the optical transition by drawing the relations $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{2/3}$, $(\alpha h\upsilon)^{1/2}$, and $(\alpha h\upsilon)^{1/3}$ as function of incident photon energy (hυ) and choosing the optimum linear portion. It is found that only the first relation has straight line region where the absorption coefficient (α) which was determined using equation (1) was of the order $10^4 cm^{-1}$, which indicates that only the direct allowed transition happen in these films. This result confirms by Henry et al and Albert et. al.[10, 25, 30] for as deposited pure Cu films. Then $E_g^{opt}$is estimated by intercepting the linear part of the absorption curve to the x-axis (hυ) for zero absorption coefficient (αhυ=0), and the magnitudes of E_g^{opt} are listed in Table 1. Figure (3a) represents $(\alpha h\upsilon)^2$ as function of hυ for as deposited CAZTSe thin films with 0.0, 0.1, and 0.2 Ag content. From this Figure and Table 1, one can be noted that the optical absorption edge of pure Cu film shifts to lower energies with increasing Ag content. This may be returned to the larger crystal size of these films and this due to the substituting of Cu with ionic radius (0.91Å) by Ag with ionic radius (1.29Å)[25]. The calculated E_g^{opt} had the similar behavior to which obtained by Gong et. al.[31], but the difference in values may be resulted from the difference in films preparation conditions, which play a great role in

determine the properties of film. The narrowing in E_g with increasing of Ag content indicates that Ag occupy substituting site[26]. While figures (3b&c) represent the effect of annealing temperature to 373K and 473K on the E_g of these films. It is clear from these figures and the same table that the value of E_g decreases with increasing the temperature of annealing and these films possess lower values of E_g than as deposited films. This may be returned to the growth of grain size during annealing process as estimated from AFM results in our earlier repot[28].

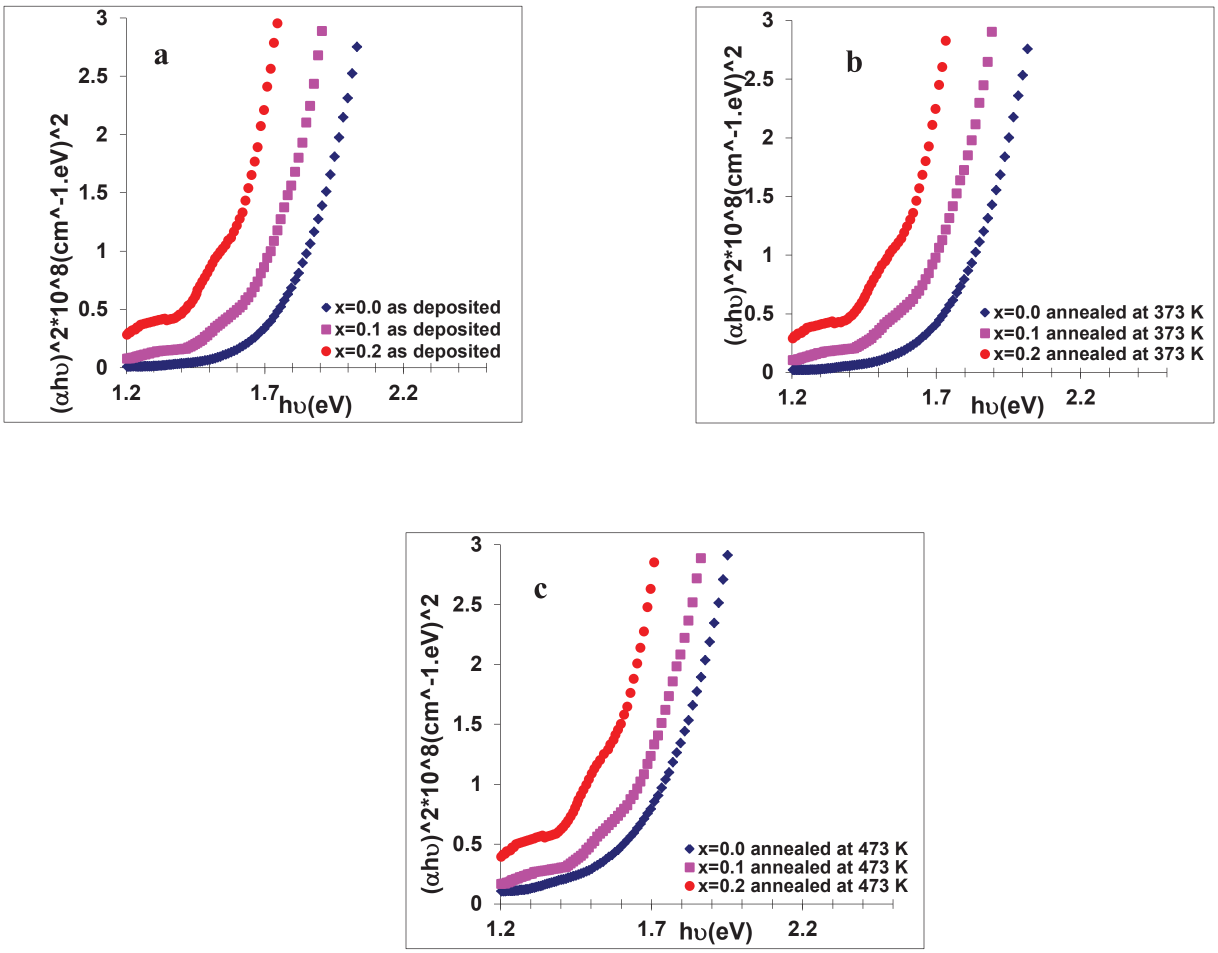

FIGURE 3. $(\alpha h\upsilon)^2$as a function of (hυ) for thin $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ films of different Ag ratios

at: (a) R.T, (b) 373K, (c) 473K.

TABLE 1. Optical energy gap of thin CAZTSe films for various Ag content and annealing temperatures.

x	Ta (K)	(eV)
0.0	**R.T**	1.75
	373	1.72
	473	1.65
0.1	**R.T**	1.61

x	Ta (K)	(eV)
	373	1.59
	473	1.55
0.2	R.T	1.54
	373	1.52
	473	1.5

Evaluating the refractive index of photomaterial is necessary for many applications especially in photodevice. So, refractive index is one of the most important optical parameters. Figure (4a,b,&c) displays the change of refractive index which was calculated from equation (2) for as deposited and annealed to 373K and 473K thin CAZTSe films with various Ag content. It is clear from this figure and Table 2 that the value of n increases with increasing Ag content and temperature of annealing. This is an expected result due to the inverse relationship between n and E_g^{opt} in semiconductor (32).

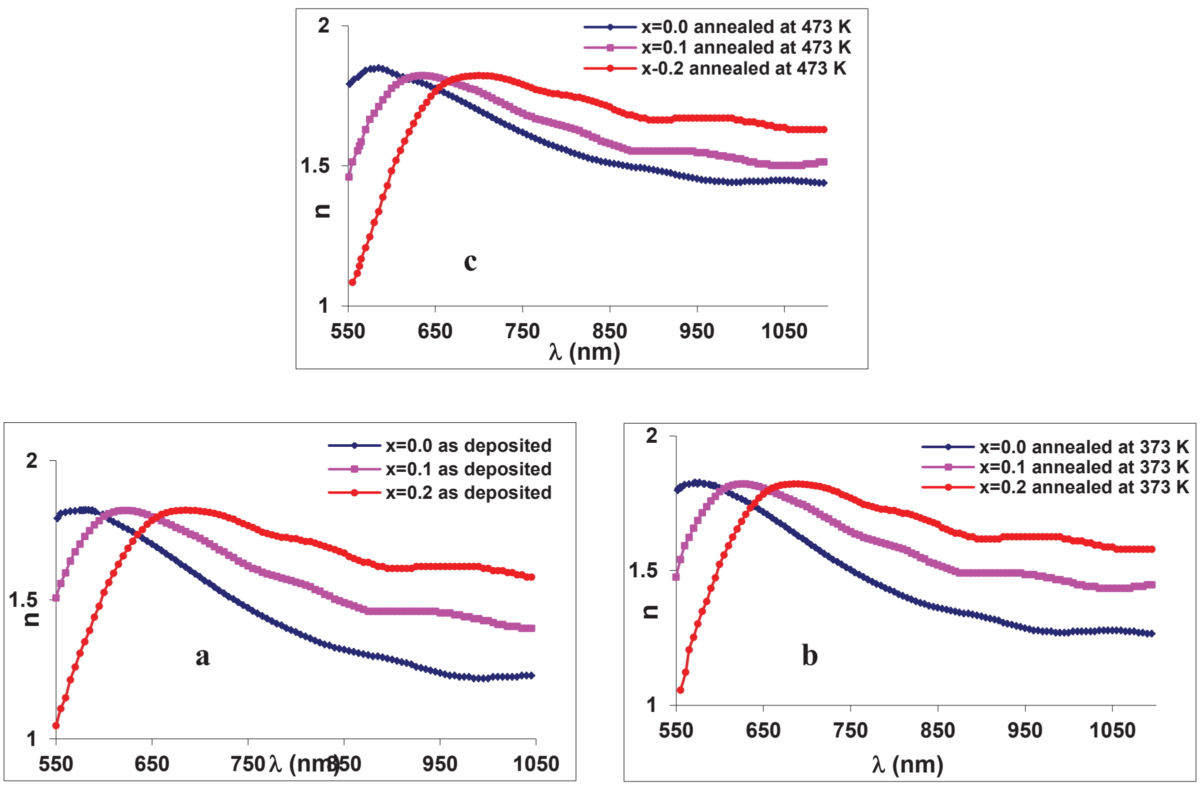

FIGURE 4. The refractive index as a function of wavelength for thin $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ films of different Ag ratios at: (a) R.T, (b) 373K, (c) 473K.

The relationship between extinction coefficient which estimated by using equation (3) and wavelength for as deposited and annealed to 373K and 473K thin CAZTSe films with various magnitudes of x is displayed in Figure (5a,b,&c). The observational from this figure that k takes the identical behavior of corresponding absorbance. So, k increases with increasing x and T_a as shown in this figure and Table 2.

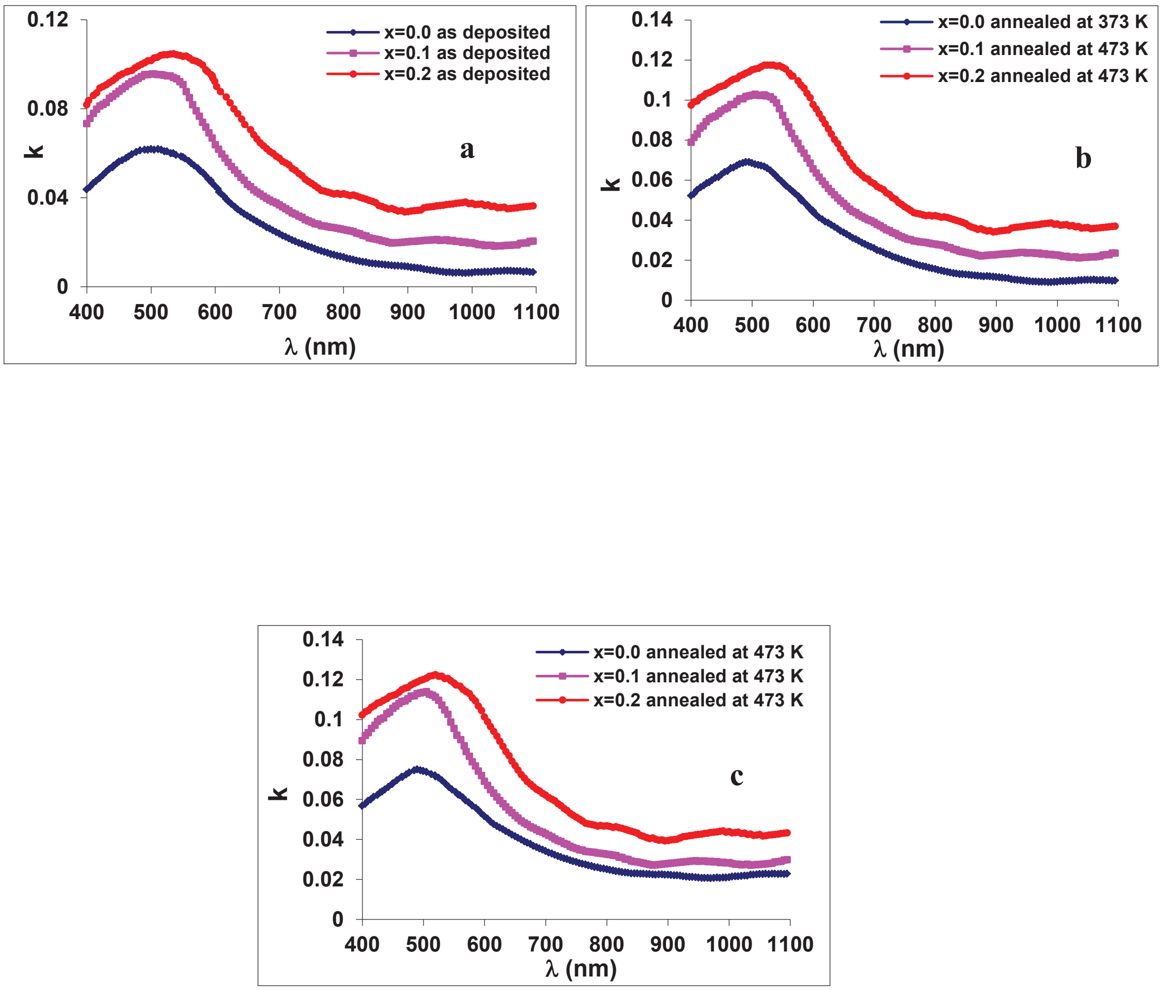

FIGURE 5. The extinction coefficient as a function of wavelength for $(Cu_{1-x}Ag_x)_2ZnSnSe_4$ films of different Ag ratios at: (a) R.T, (b) 373K, (c) 473K.

Finally, the variation of real and imaginary parts of dielectric constant with wavelength which determined by using equations (4) and (5) respectively is similar to variation of refractive index and extinction coefficient respectively with wavelength. Therefore, value of ε_r and ε_i increases with increasing x and T_a as shown in Table (2).

TABLE 2. Optical constants of thin CAZTSe films for various Ag content and annealing temperature at λ=700nm.

x	T_a(K)	n	k	ε_r	ε_i
0.0	**R.T**	1.582095	0.023909	2.502452	0.075653
	373	1.607477	0.025877	2.583312	0.083193

x	T_a(K)	n	k	ε_r	ε_i
	473	1.698108	0.034215	2.882400	0.116202
0.1	**R.T**	1.721355	0.036858	2.961704	0.126891
	373	1.737007	0.038826	3.015686	0.134882
	473	1.764682	0.042849	3.112267	0.151229
0.2	**R.T**	1.819318	0.057865	3.306569	0.210549
	373	1.819776	0.058259	3.308191	0.212037
	473	1.821808	0.062282	3.315105	0.226932

CONCLUSIONS

This paper highlights the alter in the optical properties of thermally evaporated thin CAZTSe films due to alteration of Ag dopant ratio (x) and temperature of heat treatment (T_a). Pure Cu films adopt high absorbance, low transmittance in visible region and films absorbance enhance when x and T_a increase, so silver alloying is a promising method to improve the thin CZTSe films optical characteristics to obtain appropriate absorber layer for solar cell application. Allowed direct band gap has been noted for all prepared films and its magnitude is decrease with increase x and T_a. Also it can be estimated that Ag ratio and annealing temperature had an effect on all optical constants under studied.

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