The Effect of Annealing Temperature on the Optical Properties of the a-Ge: As Thin Films

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Abstract

a-Ge: As thin films have prepared by thermal evaporation technique, then they were annealing at various temperatures within the range (373-473) K. The result of X-ray diffraction spectrum was showing that all the specimens remained in amorphous structure before and after annealing process. This paper studied the effect of annealing temperature as a function of wavelength on the optical energy gap and optical constants for the a-Ge:As thin films . Results have showed that there was an increasing in the optical energy gap (E_g^{opt}) values with the increasing of the annealing temperatures within the range of measurements due to the decrease in defect states near the bands. The refraction index , real and imaginary parts of dielectric constant and the extinction coefficient decrease with the increasing of the annealing temperatures .

Introduction

A-Ge and a-Si are well known as the most important amorphous semiconductor materials, which used as thin films and future materials in produce solar cell in wide range and complex electronic device because of their high efficiency, easy prepared and low cost that it preferred on crystalline semiconductors (1).

The optical properties measurement such that; the optical energy gap and the optical constant used to study the electronic structure, unorderied and the defects in amorphous semiconductor, so that most of researchers in the recent years tends to study this type of thin films by different prepared methods and conditions such that ;thermal evaporation(2) ,electron beam (3) ,glow discharge (4) ,and sputtering (5, 6) they deduced that the structure ,optical, electrical properties for pure and doping a-Ge depending on the preparation methods and conditions ,such that rate of deposition (7) ,thin films thickness (8) , substrate and annealing temperatures (9) ,which caused the absorption edge to shifted up or down energy(9) .

The purpose of this work to study the effects of annealing processes within temperature of the range (373-473) K on the optical energy gap, refraction index (n), extinction coefficient (k), and the real (ε_r) and imaginary parts of dielectric constant.

Optical Properties

The optical properties arise from the electromagnetic energy absorbed or emitted as free carriers undergo inter sub band (between mini bands) transition.

In semiconductors, there are several processes that may result in the absorption of an incident photon: as shown in Fig.(1) Interband transition (a) may occur when a resonant photon interacts with a valence electron, exciting it to an unoccupied level in the conduction band. Charge transfer transitions (b) may occur in which a photon either excites a valence electron into an empty acceptor state, or excites a donor electron into an empty conduction band state .Intraband transition (c) may also occur in which a valence electron is excited into an unoccupied valence band state, or a conduction electron is excited into an unoccupied conduction band state (9) .

Fundamental Absorption

The fundamental absorption refers to band-to-band or to excitation transitions (i.e. to the excitation of an electron from the valence band to the conduction band. It is manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor (10) .

The transitions are subject to certain selection rules; therefore the estimation of the energy gap from the "absorption edge" is not a straight forward process- even if competing absorption processes can be accounted (10). The dominant feature of the energy dependence of the absorption coefficient is the onsets of absorption near the region of interband transition from valence to conduction bands. The energy dependence of α near the band edge for band to band and exciton transition could described by Tauc formulas: (11)

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

Where ,B is a constant inversely proportional to amorphousity , hν is the photon energy (eV), E_g^{opt} is the optical energy gap (eV), α is the absorption coefficient ,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, as illustrated in Fig.(2):

1-Direct Transitions:

It defined as the electron transitions that occur from band to band by "vertical transition" which involves photons in transition and the momentum of the crystal must conserved.

A-Allowed direct transition:

This transition was takeplace in crystalline and polycrystalline semiconductors. In this transition the electron is excited from the top of the valence band to the bottom of the conduction band with absorption of photon, has the same value of k, such that (k=0), and (Δk=0) given by:

$\alpha h\nu = B\,(h\nu - E_g^{opt})^{1/2}$ ------------------------- [2]

B-Forbidden direct transition:

This occurs in some materials, quantum selection rules forbid direct transition at k≠0, but allow them at Δk=0, the absorption coefficient is given by:

$\alpha h\nu = B'(h\nu - E_g^{opt})^{3/2}$ -------------------------------------- [3]

Where, B' is a constant.

2-Indirect Transitions:

When a transition requires a change in both energy and momentum, a double, or two-step (allowed and forbidden), process is required because the photon cannot provide a change in momentum (Δk≠0). Momentum conserved via a phonon interaction, that: (11)

$\alpha_i(h\nu) = \alpha_e(h\nu) + \alpha_a(h\nu)$ -- [4]

Where α_i: is the absorption coefficient due to indirect transition.

α_e: is the absorption coefficient due to phonon emission.

α_a: is the absorption coefficient due to phonon absorption.

When $h\nu > E_g^{opt} - E_p$ where E_p is the phonon energy

Then $\alpha_e=0$, so that we have phonon absorption and the absorption coefficient for this transition are given by:

$\alpha_a(h\nu) = A\,(h\nu - E_g + E_p)^2 / [\exp(E_p/k_BT) - 1]$ -------------- [5]

When $h\nu > E_g^{opt} + E_p$

Then $\alpha_a=0$, so that phonon emission and the absorption coefficient for this transition are given by:

$\alpha_e (h\nu) = A'(h\nu-E_g-E_p)^2 / [1-\exp (E_p /k_BT)]$ ------------ [6]

Where, A, A' are constants. The Optical Constants:

The optical behavior of a material generally utilized to determine its optical constant [refractive index (n), extinction coefficient (k) and, real (ε_r) and imaginary parts (ε_i) of dielectric constant].

The complex index of refraction (n_c) defined as (11):

$n_c=n-ik$ --- [7]

And it's related to the velocity of propagation (v) by:

$v=c/ n_c$ --[8]

Where, c is the velocity of light in vacuum. The real part of refraction index values can calculate from the formulas (12) :

$n= \{[4R/(R-1)]-k^2\}^{1/2} - [(R+1)/(R-1)]$ ----------------------[9]

Where, R is the reflectance.

The absorption coefficient (α) related to k by:

$\alpha=4\pi k/\lambda$ --[10]

Where, λ is the wavelength of the light in vacuum.

The dielectric constant can introduced by: (91)

$\varepsilon=\varepsilon_r-i\varepsilon_i$ --[11]

Where, $\varepsilon_r=n^2-k^2$ --[12]

$\varepsilon_i =2nk$ --- [13]

Where ε_r, ε_i, the real part and imaginary of the dielectric constant respectively.

Experimental Work

A-Ge:As thin films were preparing by thermal evaporation in vacuum about 10^{-6} torr using Balzer BAE370. The rate of deposition was about 0.5 nm/sec and film thickness was approximately 250nm, which measured by quartz crystal monitor. The films have been doping with 2.5% of As, they were deposited on cleaning glass substrate at R.T (303K) and annealing under vacuum at different annealing temperatures (373,423,473) K.

The transmittance (T), absorbance (A) for the thin films as function of wavelength in the range from 200nm to 1100 nm measured using Shimadzu UV-160 Spectrophotometer,the optical constant have been calculated using computerized program.

Result and Discussion

The amorphous structure of the films confirmed by x-ray diffraction examination methods for all specimens before and after annealing using Philips x-ray Diffractometer as shown in Fig.(3).

The import of studies the optical properties of annealed a-Ge: As thin films was to determine the limits of varied the optical energy gap (E_g^{opt}) with the annealing temperature within the range that keep it in amorphous structure.

Figs. (4) illustrate the variation of $(\alpha h\upsilon)^{1/2}$ against photon energy for a-Ge:As thin films annealed at different temperature (373-473) K .

The optical energy gap could be determined by the intercept the linear part of the curve with the x-axis at α=0.

We can deduce from Fig.(4) that the optical energy gap was indirect energy gap . Table (1) show that the optical energy gap increased with the increasing of annealing temperature within the range of measuring wavelength, and this due to the decreasing in the density of state and disorderness in the atomic bonding between the neighbor and this will causes decreasing in the expansion of the tail states near the band edge and saturated of the dangling bonds.

Fig.(5) Shows the variation of the refraction index (n) with wavelength (A) within the range of annealing temperature, it was appear that there was a conformable of curves at wavelength around 960 nm approximately.

The refractive index increase in the range(680-1000) due to increase the packing density .

It appears from Fig. (6) which shows the variation of the extinction coefficient (k) with measured wavelength at various annealing temperature ,that the extinction coefficient has low value for different annealing temperature at high values of wave lengths while it has high values for the same annealing temperature at low values wavelengths. Fig. (7) Shows the variation of the real part of the dielectric constant with wavelength, we noticed that there was a peak at wavelength of range (960-980) nm ,the real part increase with wavelength for various Ta in the range (660-1000) due to depended on n^2 value according to equation (12) because k^2 has low value compare with k. Fig. (8) shows the variation of the imaginary part of dielectric constant with wavelengths, there was a peak at wavelengths of range (760-800) nm, within the same annealing temperature range, also its value comparable with k values according to equation (13) in the range (850-1000) nm.

Conclustion

a- Ge: As thin films prepared by thermal evaporation, which have annealed at annealing temperature of the range (373-473) K expresses the following properties:

1- They kept in amorphous structure within this range of annealing temperature.

2-There was shifting in the peak of the optical constants as a function of wavelengths within the measured range of annealing temperature to the shorter wavelength due to the increases of the optical energy gap . .

3- There was an increasing in the k values with annealing temperature for all range of the wavelengths, due to increasing in the absorption coefficient with the increasing of the annealing temperature.

4- There was a peak of refractive index (n) curves at wavelength around 960 nm approximately.

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Table (1): illustrate the values of Eg as a function of Ta.

Ta(K)	$E g^{opt}$ (e V)
R.T	0.840
373	1.175
423	1.187
473	1.200

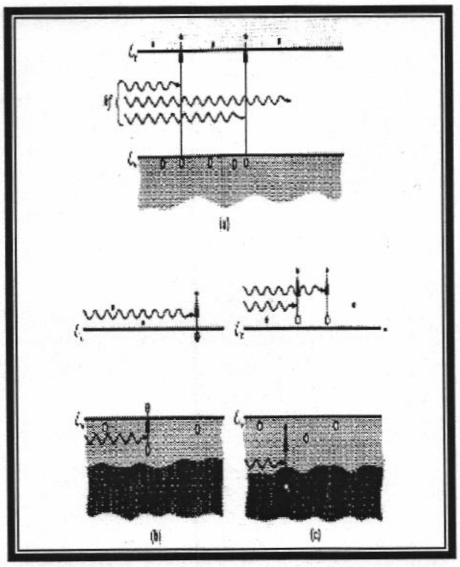

Fig. (1) The possible absorption processes in a semiconductor a) Interband, (b) Charge Transfer, and (c) Intraband (9)

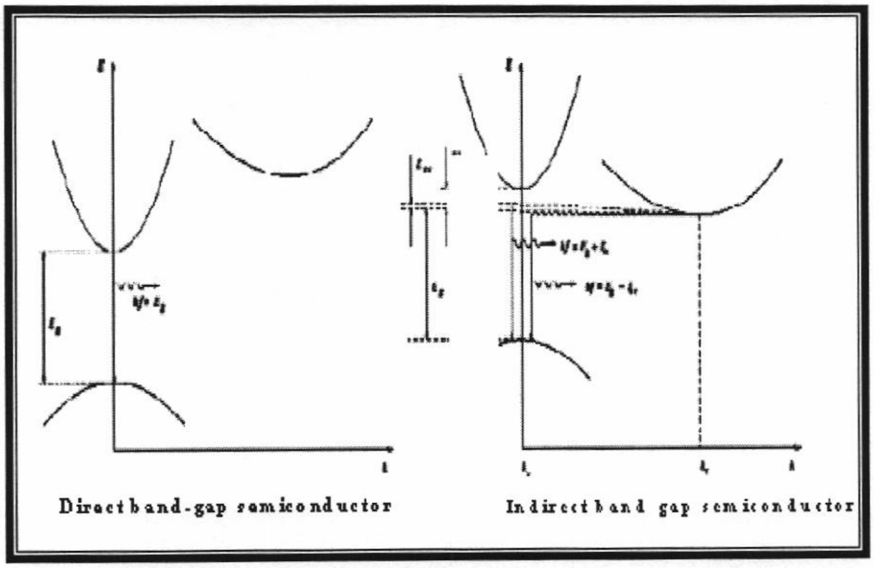

Fig. (2): Direct and indirect band gap semiconductor (9)

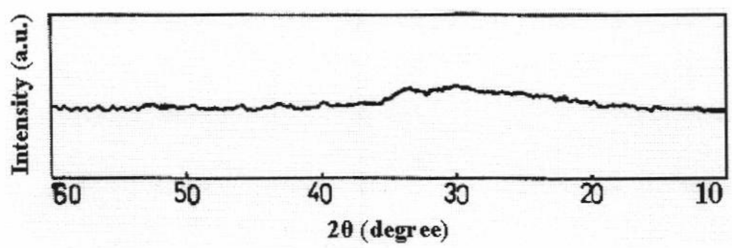

Fig.(3) The X-ray diffraction of Ge:As films

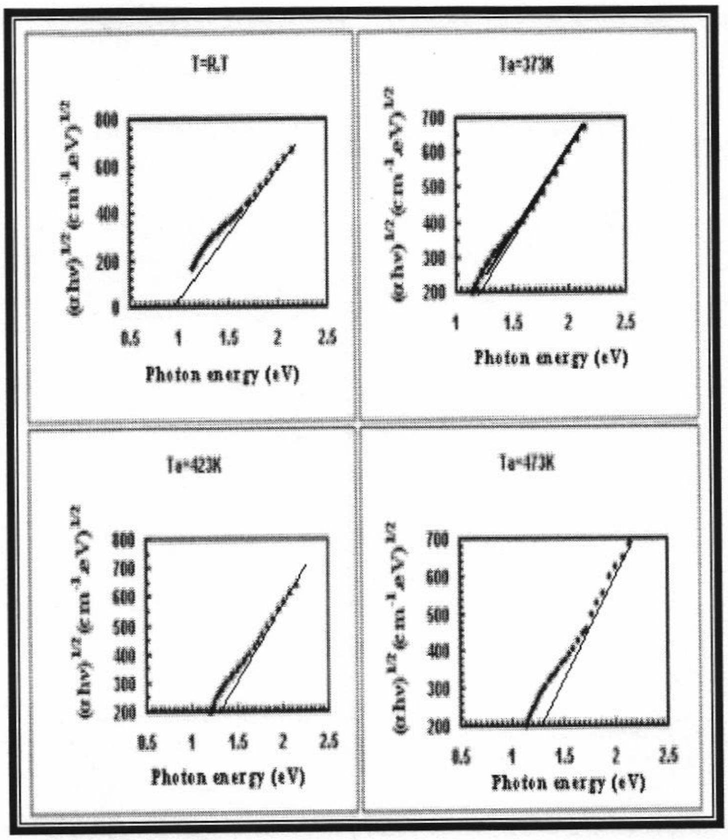

Fig.(4) The variation of $(\alpha h\nu)^{1/2}$ with photon energy for a-Ge:As thin films for different annealing temperatures

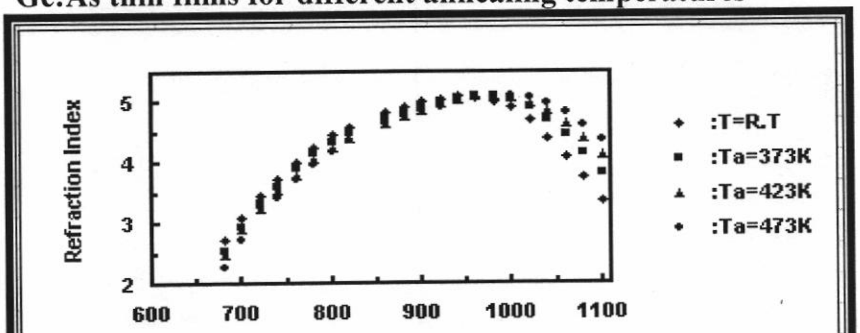

Fig.(5) The variation of refraction index verse wavelength at different annealing temperatures

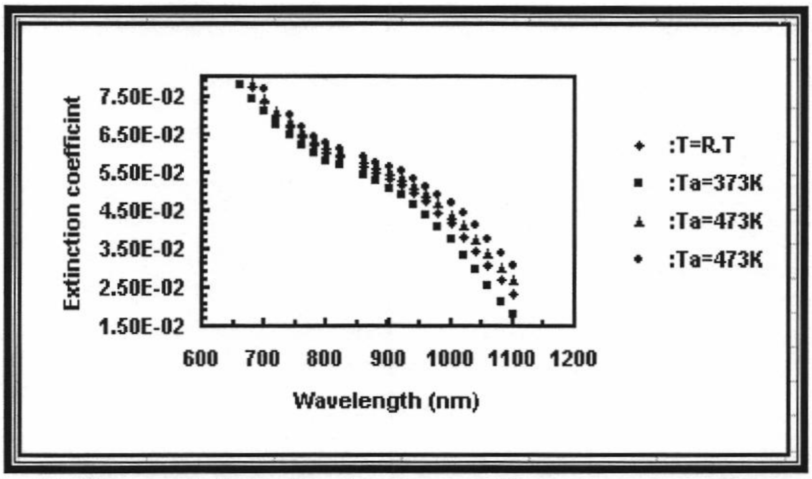

Fig.(6) The variation of extinction coefficient verse wavelength at different annealing temperatures

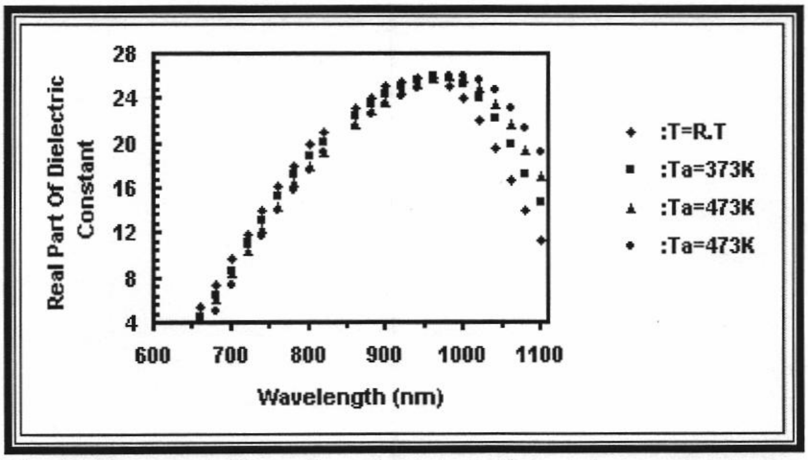

Fig.(7) The variation of real part of dielectric constant verse wavelength at different annealing temperatures

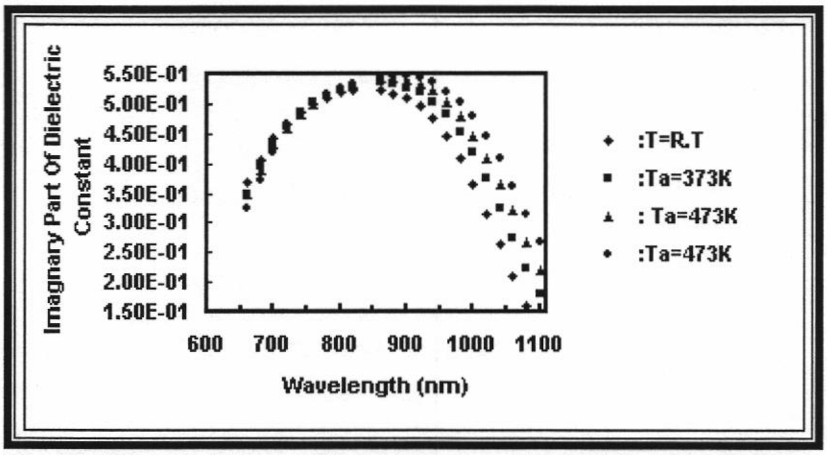

Fig.(8) The variation of imaginary part of dielectric constant verse wavelength at different annealing temperatures

تأثير التلدين على الخواص البصرية للأغشية a –Ge:As الرقيقة

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المستخلص

تم تحضير أغشيةGe:As– a الرقيقة بتقنية التبخير الحراري . ومن ثم لدنت الى مختلف درجات الحرارة ضمن المدى .K (473–373) ان نتيجة طيف حيود الأشعة السينية بينت ان النماذج عشوائية التركيب قبل وبعد التلدين . ان البحث يدرس تأثير درجات حرارة التلدين كدالة للطول الموجي على فجوة الطاقة البصرية والثوابت البصرية لأغشيةGe:As– a الرقيقة . لقد بينت النتائج ان قيم فجوة الطاقة البصرية E_g^{opt} تزداد مع زيادة درجات حرارة التلدين ضمن مدى القياس نتيجة لنقصان حالات العيوب قرب الحزمة . ان معامل الانكسار والجزء الحقيقي والخيالي من ثابت العزل ومعامل الخمود يقل مع زيادة درجة حرارة التلدين .