Effect of Annealing Temperature on the Crystallographic and Optical Properties of ZnO Films

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Abstract

ZnO Polycrystalline films were prepared on glass substrate by solvent evaporation at 25°C, and post annealed in air at range of annealing temperatures of (100, 200,300°C) for 1 hour. The samples were characterized by analyzing the structural and optical properties. X-Ray diffraction results reveal that the deposited ZnO films are polycrystalline in nature with cubic structure having (100) plane as a preferred orientation. The structural parameter such as the grain size, dislocation density, number of crystallite per unit area and stress were calculated for all films. The result shows that the change in deposited films properties is close to that of single crystal ZnO properties, with increasing the annealing temperature. Various optical parameters such as transmission, absorption coefficient and band gap energy have also been evaluated, the result of optical properties shows a direct allowed transition.

تأثير درجة حرارة التلدين على الخصائص البصرية ZnO والميكانيكية لأغشية اوكسيد الزنك

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الخلاصة

تم ترسيب أغشية اوكسيد الزنك على قواعد زجاجية باستعمال تقانة الترسيب من المحلول . بعد الترسيب تم أجراء عملية التلدين الحراري للاغشية بدرجات حرارة (١٠٠,٢٠٠,٣٠٠) درجة مئوية وبزمن ترسيب (١) ساعة .من خلال فحوصات حيود الأشعة السينية تبين أن الأغشية متعددة البلورات وذات توجهيه مثلى للمستوي (100) ، كذلك تم قياس حجم الحبيبات ،كثافة الانخلاعات ، عدد البلورات لوحدة المساحة والإجهاد٠ تم اجراء الفحوصات البصرية كفحوصات النفاذية ومعامل ألامتصاص،ومن خلالها تم حساب قيمة فجوة الطاقة البصرية وتبين أنها ذات نوع انتقال مباشر . من خلال هذه القياسات يتضح لنا ان خصائص أغشية اوكسيد الزنك تقترب من خصائص البلورة الأحادية لاوكسيد الزنك مع زيادة درجة حرارة التلدين .

1-Introduction

The deposition of Transparent Conductive Oxides (TCO) is characterized by superior optical and electrical properties, which make them attractive in production of transparent electronic devices. Among all(TCO) material (ZnO) has emerged as one of the most promising materials due to its optical and electrical properties such as high chemical and mechanical stability, low cost, abundance, non –toxicity and easy fabrication[1-3]. ZnO is a wide direct band gap semiconductor (3-3.7eV) with a hexagonal crystal structure of Wartize and a large excition binding energy of 60 meV [4-7]. These properties make ZnO as an important material in many applications such as thin film gas sensors [7-9], varistors [10,11], and phosphor for colour displays[12,13]. A variety of methods have been reported for the

preparation of ZnO thin films like films deposited by thermal evaporation [14,15] rf sputtering [16-18], chemical vapor deposition [19,20], laser ablation [21], spray paralysis [22,23],and magnetron sputtering [24,25].

In this work we have studied the effects of post annealing temperature on the optical and structural properties of ZnO films prepared by solution evaporation.

2- Experimental

2-1 Sample preparation

1- The glass substrate was cut in dimension (2.3x 2.5Cm).
2- The glass substrate immersed was in (CrO_3) for 3 hours to remove the impurities.
3- The glass substrate was then immersed in deionized water for 2 hours, and then kept it in a hot air to become dry.

2-2 Deposition mechanism

ZnO powder (0.1gm) from (DEMANE Radial Deform) was dissolved in (100ml) of deionized water at 25 ºC. After totally dissolving of the ZnO powder, the solution was placed inside a beaker with surface area of ($5cm^2$), the glass substrate was placed in the bottom of the beaker. Precipitation of small crystallites occured rapidly after the evaporation of the excess water, and thin layers (typically~ $2\mu_m$ thick) were obtained on the glass substrate.

2-3 Thickness measurements

Film thickness was measured by weight method using sensitive electrical balance of mettler AE -160, with precision reaching 10^{-4}gm. The following mathematical relationship is adopted.

Thickness= $\Delta m/ \rho_f * A_f$

where Δm= the deposited thin film weight, which is equal to the difference between weight of the glass slide after and before the deposition process**.** $\boldsymbol{\rho_f}$ is the ZnO density and A_f is the area of the glass substrate.

2-4 Crystallographic structure:

The diffraction spectra of ZnO films were obtained by scanning (2 θ)in the range (30-38) using CU-Kα (Philips pw1840) which has the following characteristics : the CU-Kα with (1.54A) wave length and scanning speed (3degree/min). The crystallite size (D) in the film has been calculated using scherr's formula from full width at half maximum (β) [26].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

The dislocation density (δ) has been evaluated using the formula [27].

$$\delta = \frac{1}{D^2}$$

The films strain (ξ) was calculated using the relation [27].

$$\beta = \frac{\lambda}{D\ \cos\theta} - \xi \tan\theta$$

The number of Crystallites / unit area (N) can be obtained using the relation[27]

$$N = \frac{1}{D^3}$$

2-5 Optical measurement:

Optical transmission measurement was performed at room temperature (300-900)nm using Phenix-2000uv-vis spectrophotometer. Optical band gap value was deduced from the extrapolated intercept of $(\alpha h\nu)^2$ versus (hν). Absorption coefficient (α) was calculated from the transmission spectra using Beer- Lamberts law [28].

$$\alpha = \frac{1}{d} \ln \frac{1}{T}$$

where α= the absorption coefficient. d=the film thickness, T=the transmission of the film.

3- Results and discussion

3-1 Crystallographic structures

The diffraction spectra of ZnO films were obtained by scanning 2θ in the range 30º-38º. Among all possible orientations films was deposited at 25ºC and annealed at(100-200ºC) ,the (101),(002),(100) planes show preferential orientation, but for film annealed at (300ºC)

the two planes (101),(002) have disappeared and only(100) plane appears with highly orientation as shown in Fig(1). This indicates that the plane (100) is the preferred orientation plane for ZnO films especially at highly annealing temperature, so we will focus all our calculation on the mechanical properties of ZnO films from(100)plane. Fig. (2) shows the variation in the intensity of (100) plane with annealing temperature. It is very clear that the intensity increases with annealing temperature which confirms the enhancement in the film crystallinty. Fig.(3) reveals the decreasing in FWHM (β). With annealing temperature ,this result is in parallel with that of Fig.(2).

3-2 Crystal size

Fig(4) shows the relationship between the crystal size of ZnO (D) with annealing temperature. From the figure we can see that the crystal size of ZnO film increase with increasing annealing temperature. We think this is due to the incorporation of small crystal size to make a large crystal at high temperature. This result is confirmed in Fig(5) which shows the decrease in the number of crystallite / unit area with increasing annealing temperature.

Fig(6) shows the decrease in the dislocation density of ZnO films with increasing annealing temperature, because the annealing temperature plays a remarkable role in reducing the defects in the film and contributes to increasing the crystal size. For the same reason the strain in the film will decrease with increasing annealing temperature as shown in Fig(7). This means that the characterization of ZnO films will approach to that of a ZnO single crystal with increasing annealing temperature.

3-3 Optical properties

3-3-1 Transmission spectra

Different transmission spectra were obtained for annealed ZnO films at different temperatures, the spectra shows a decrease in the transmission with increasing annealing temperature for wave length shorter than the adsorption edge(360nm), while for longer

wavelengths the transmission increases with increasing annealing temperature as shown in Fig(8). This increasing in transmission is probably due to the large grain polycrystalline ZnO films

3-3-2 Absorption coefficient

Fig(9)shows the absorption coefficient curves as a function of the annealing temperature. The sharp decrease in (α)is clear with increasing(λ), also (α) increases with increasing annealing temperature. This increase in (α) may be due to the larger crystallite size of the prepared ZnO films.

3-3-3 Optical band gap

Fig (10) shows the values of the optical band gap deduced from the extrapolation of the straight line. The band gap values increase from 3.29-3.37 eV with increasing annealed temperature increase from 100 to 300°C .For higher annealed temperature the band gap approaches 3.37eV. The increasing in band gap with increasing annealing temperature could be attributed to the reduction in the defects, and to the increasing in the particle size which leads to stabilization of the band gap at 3.37eV.

Conclusion:

The structural and optical properties of ZnO films grown on glass substrates by solution technique change with increase in annealing temperature.The crystallite size increases with increase annealing temperature ,while the strain, dislocation density and the number of crystallites/unit area will decrease .The optical band gap also increase with increases annealing temperature approaching to the same value of ZnO single crystal .

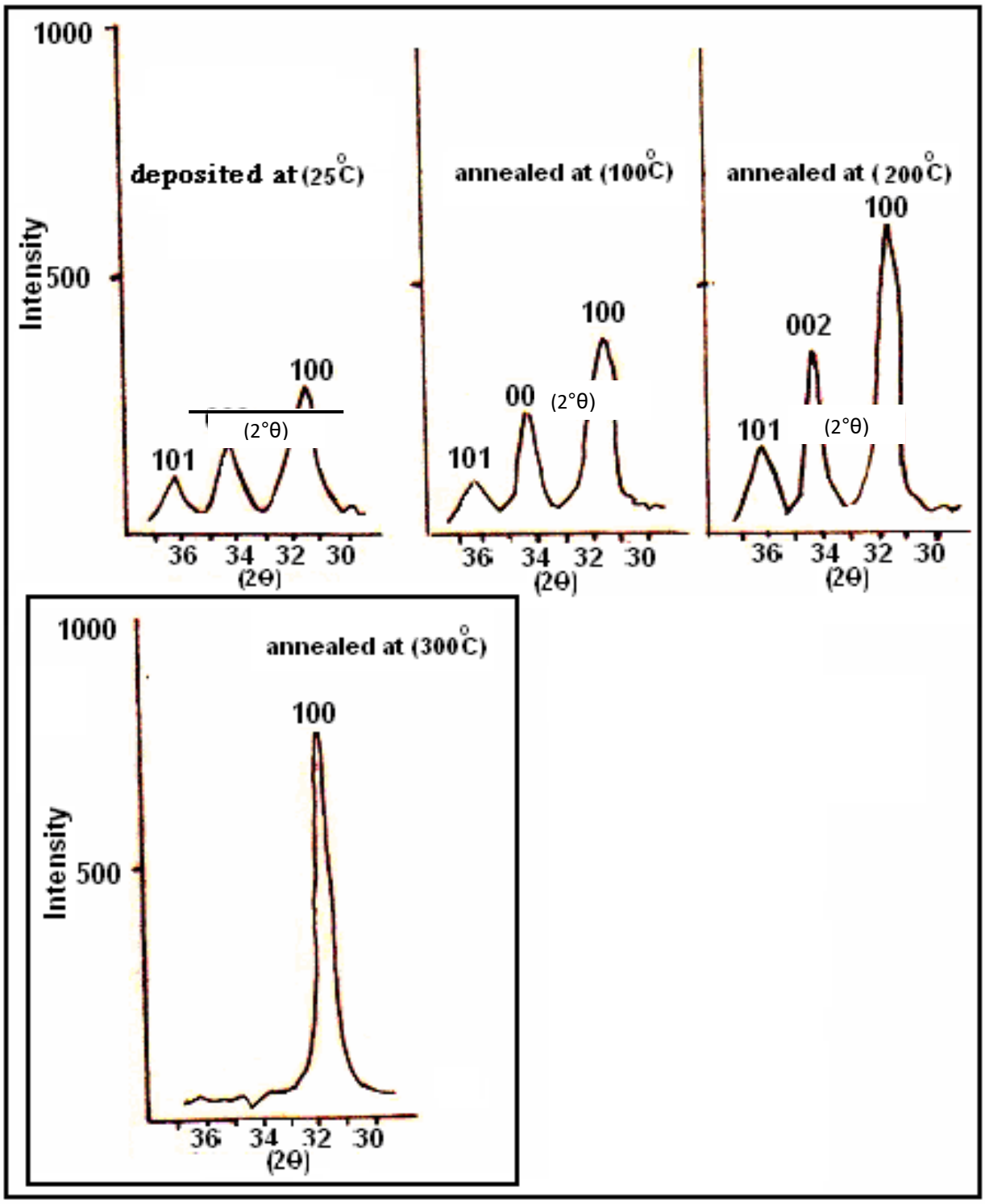
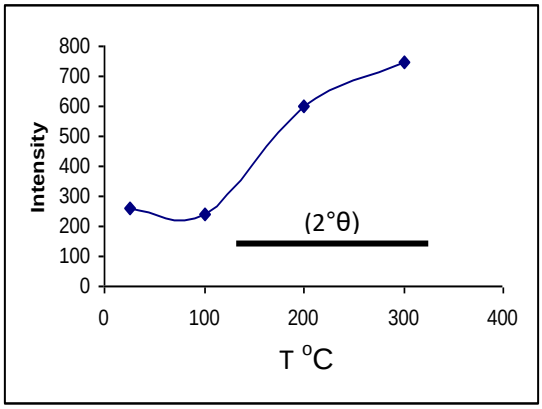
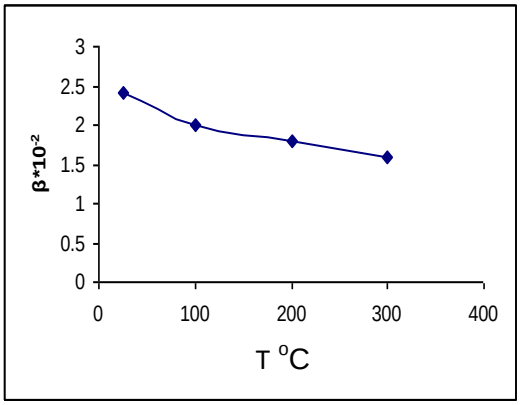


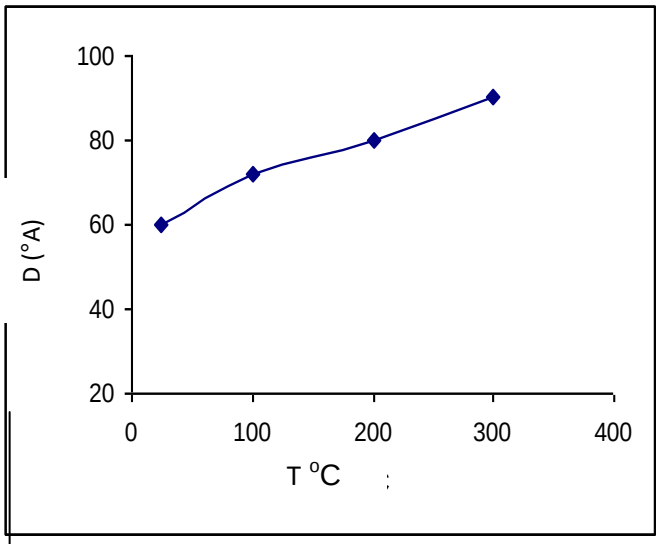
Fig (1) The X-ray diffraction of ZnO films annealed at different temperatures



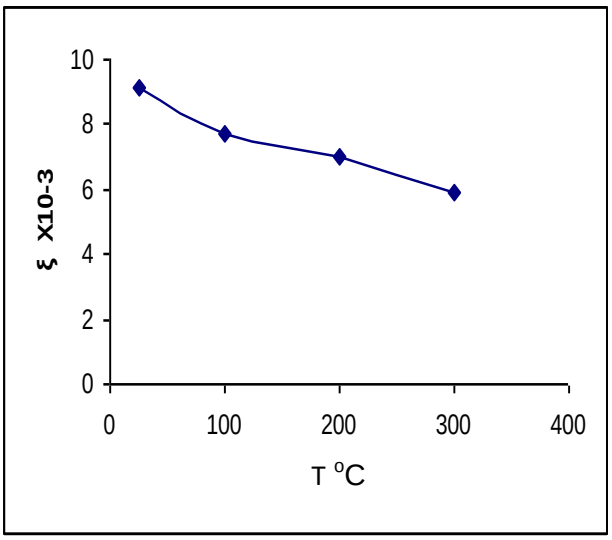
Fig(2) Variation in plane intensty with annealing temperatures



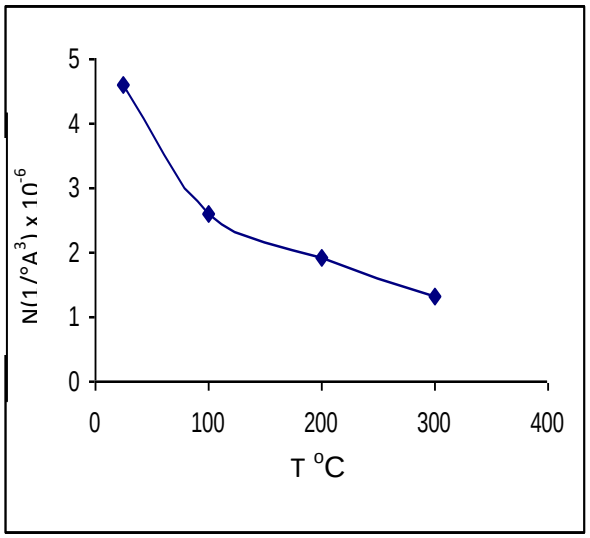
Fig(3) Variation in FWHM(β) with annealing temperatures



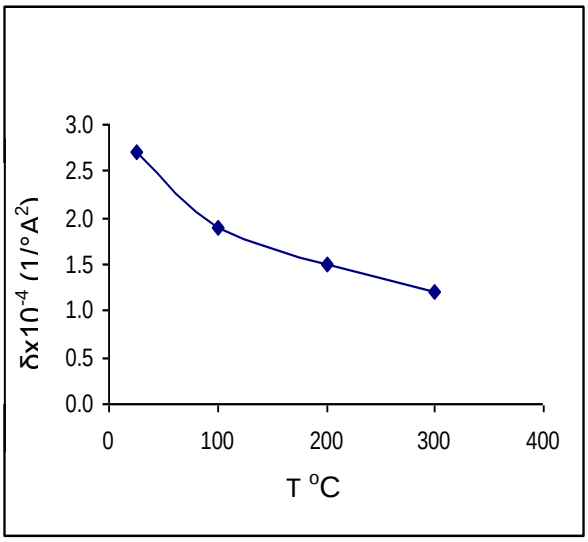
Fig(4) Variation in crystal size with annealing temperatures



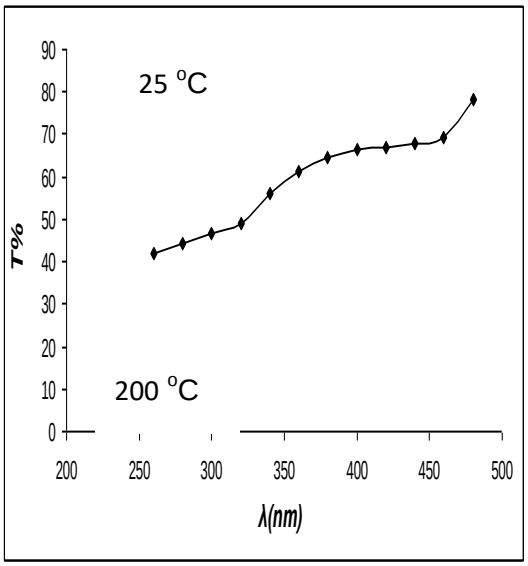
Fig(7) Variation in strain with annealing temperatures



Fig(5) Variation in number of crystallite unit area with annealing temperatures



Fig(6) Variation in dislocation density with annealing temperatures



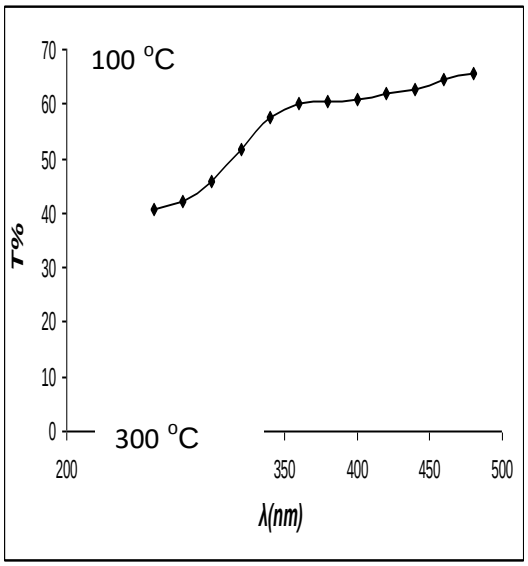


Fig (8) Optical transmission spectra of annealed ZnO films

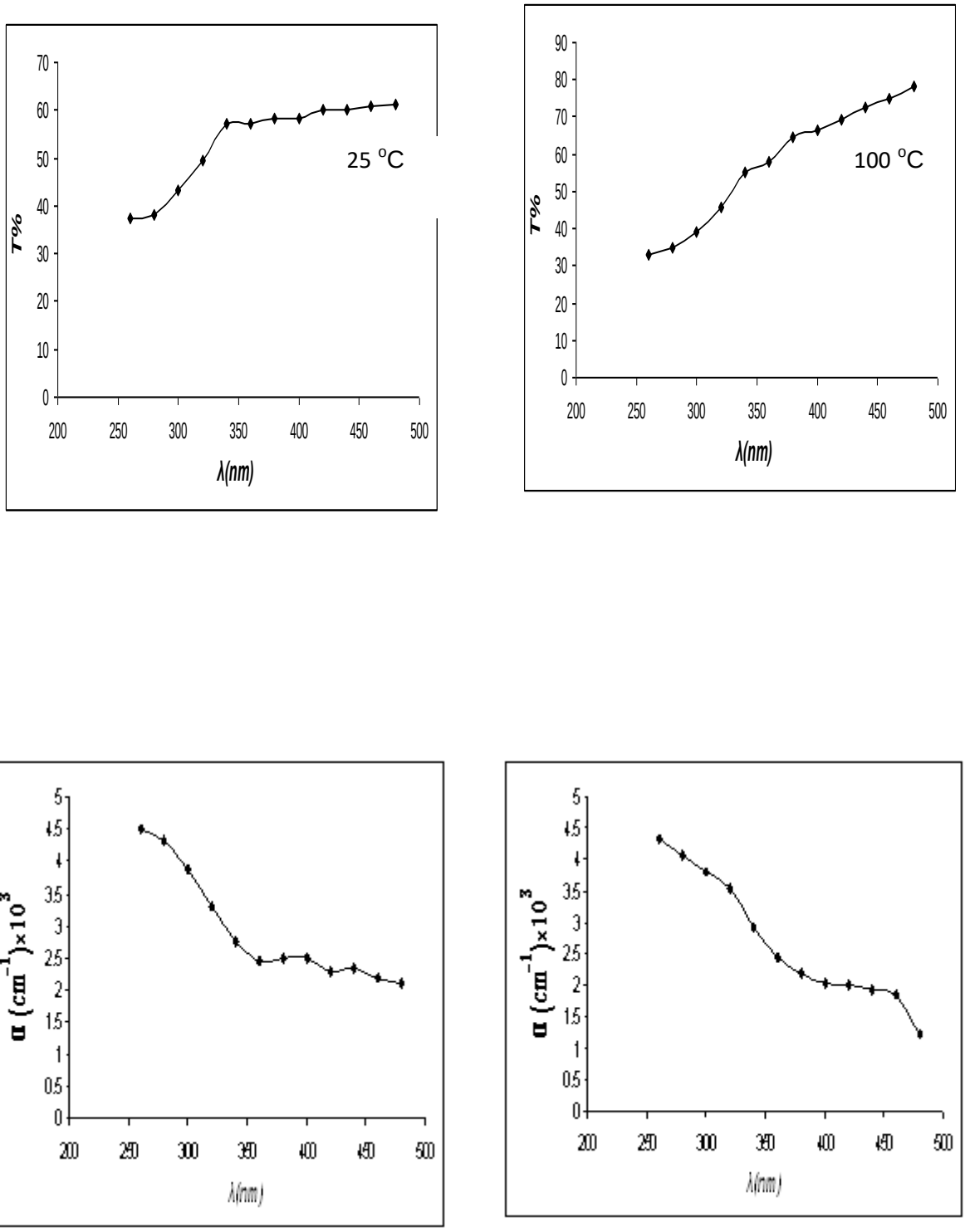


Fig (9) The absorption coefficient of annealed ZnO films

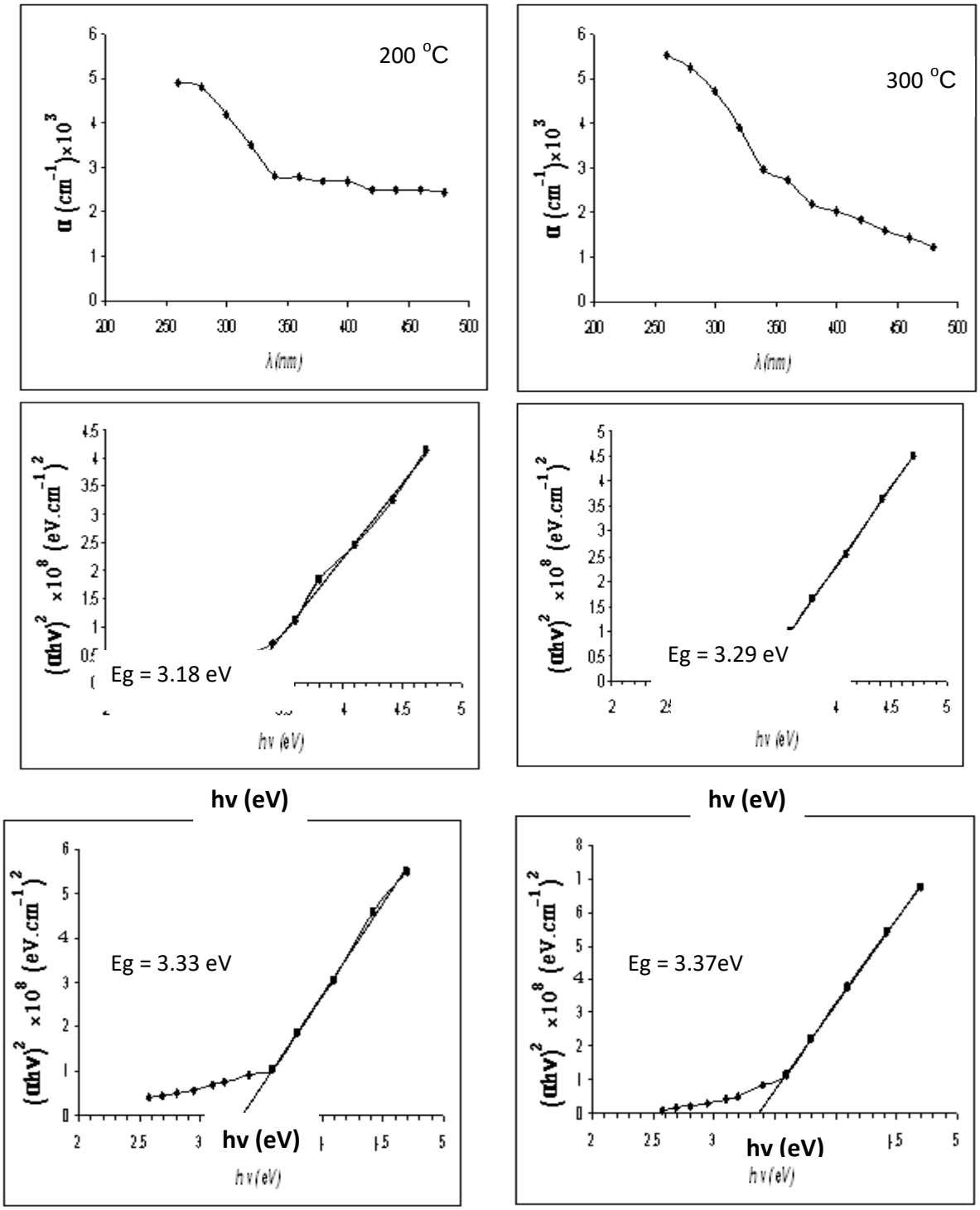


Fig (10) The variation in band gap of ZnO films with annealing temperatures

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