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Doping effect by SiO₂ on optical properties of ZnO Thin Films Prepared by pulsed laser depositions (PLD) technique

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ABSTRACT

In this paper, Zinc oxide was dopped by various concentrations (5,10,15,20,25) % wt, silicon oxide The mixture was deposited on glass substrate by laser pulse deposition at room temperature to obtain (Zn_2SiO_4) thin films. The optical properties of thin films prepared on spectral absorption and transmission recording were studied at the wavelength range (200- 1100) nm. Some of the optical constants, including absorptance, transmission, absorption coefficient, and energy gap are calculated before and after annealing at ($400°C$) for (1 hr). Absorptance values and absorption coefficient increase after doping and transmission and energy gap decreases after the doping. Absorbance values and absorption coefficient decreases after annealing and transmission and energy gap increase after the annealing.

1 - Introduction

Thin films are one of the most technologically advanced fields and the process of preparing thin films of the 19th century was first conducted in 1852 by Bunsen and Grove, which used the electrostatic deposition method to prepare thin films. Faraday also managed to prepare the thin films by thermal evaporation by moving an electric current in a metal wire and heating it to the temperature at which it evaporates. [1, 2]. The term thin films is used to describe one or several layers of atoms of a substance whose thickness does not exceed one micron. Because the thin films layer is thin, thay are deposited on different materials known as base. Bases. and substrate depends on the nature of the study, such as glass, silicon and minerals [3,4]. Thin film technology is one of the most important technologies that contributed to the development of the semiconductor study and gave a clear idea of many of its properties. Thin films are used in many different fields. They are used in the manufacture of various components of microelectronic devices, reagents, magnetic storage equipment, inverter filters, inverter and inverter coatings. They are also used in the manufacture of micro circuits, electrical circuits for electronic microscopes and in the manufacture of capacitors and rectifiers. Because of their small size and light weight, they are used in digital computers. [5]. Zn_2SiO_4 (willemite) is a long known material which still retains its place among the best inorganic phosphors [6]. Having different crystal phases and being sensitive to doping by transition metals and rare earths it can emit light at different wavelengths in the visible and near IR range. In the past years there were successful attempts to synthesize nano-phase of Zn_2SiO_4 using both solid state techniques [7]. Optical properties were studied for the purpose of preparation of optical detector

2- Experiment part

The ZnO powder was mixed with SiO_2 powder by stuitable concentrations ratios of (1,2,3,4,5) %, respectively. The proportions of the powders were weighed using a sensitive electronic balance. The powders were then mixed into mixing machine Type of Spex mixer for (5) Minutes and then the powders were blended with a hydraulic press of the type to obtain the tablet of the compound (Zn_2SiO_4). And sintering the tablet in a tube electric furnace at a temperature of ($1000°C$) for two hours and after the process of sintering left the tablets to cool. The process of deposition of films according to ratios was accomplished within a vacuum chamber in the laser system under pressure 10^{-3} Torr and the laser energy

was (1000) mJ, which is the appropriate energy for deposition .After the thin films were prepared, the films were annealing for an hour in a 400˚C in a tube electric furnace . The chemical Materials used were brought from American origin by high purity(99.999) .Glass slides were used with German-made dimensions (26 X 76 X 1). These glass plates were cleaned using the following steps:1-Wash the slides or glass bases with water and detergent powder and apply with a clean, soft cloth to remove the oil stains. 2-Immerse glass slides in high-purity ethanol for 10 minutes. 3- Wash slides with distilled water for 30 minutes. 4- Incubate slides in acetone for 15 min. 5- Place slides in plastic folders, and save them until they are used. The optical measurements of(Zn_2SiO_4) thin films depend on, thickness, homogeneity, structure, used materials and the preparation

conditions. The measured were cary out by using UV/ Visible SP-8001 spectrophotometer at wavelength (200 -1100) nm.

3- Results and discussion

3-1-Absorptance.

Fig (1),(2) show that absorbance are increasing by increasing the rate of doping before and after annealing. This is due to the development of donor levels of silicon oxide impurities within the energy gap near the conductive band this would reduce the energy gap of the deformed films, lead to the deviation of the absorbance edge towards the long wavelengths, this increasing in the absorbance valuo of (Zn_2SiO_4) in the visible region. This results agree with references [8] .
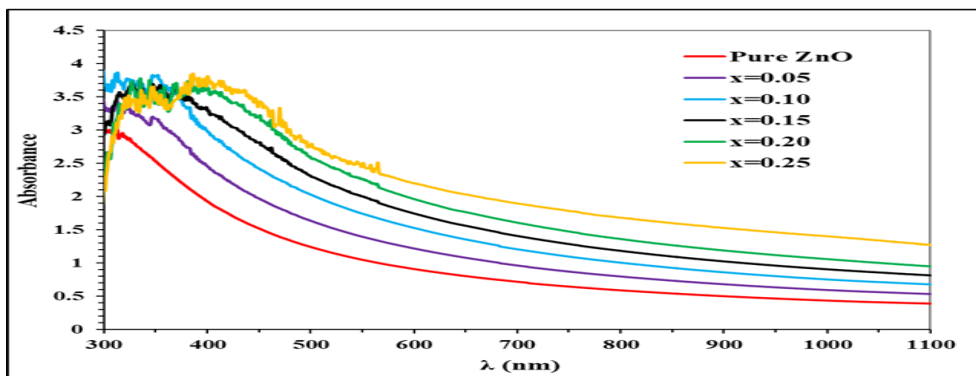

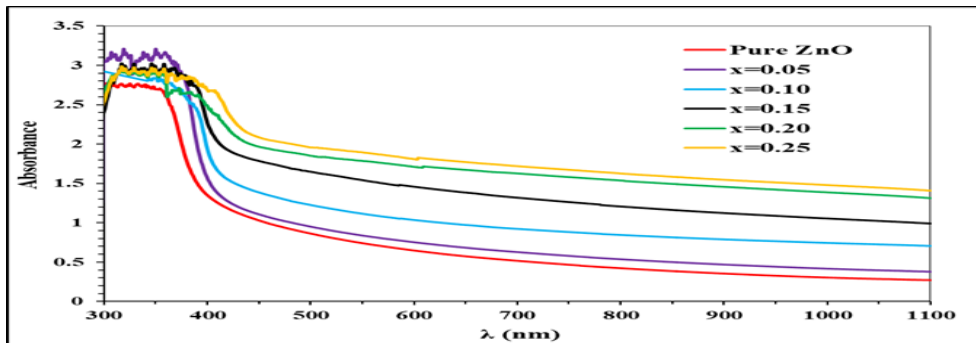**Fig (1)) Absorbance for Zn_2SiO_4 with different ratio before annealing**

Fig (2))Absorbance for Zn_2SiO_4 with different ratio after annealing

3-2-Transmission .

Fig (3),(4) show that transmission decrease before and after doping and before and after annealing the reduced value of films transmission depends on

flattening deformities, concentration centers, and photon-falling energy. This results agree with references [9] .
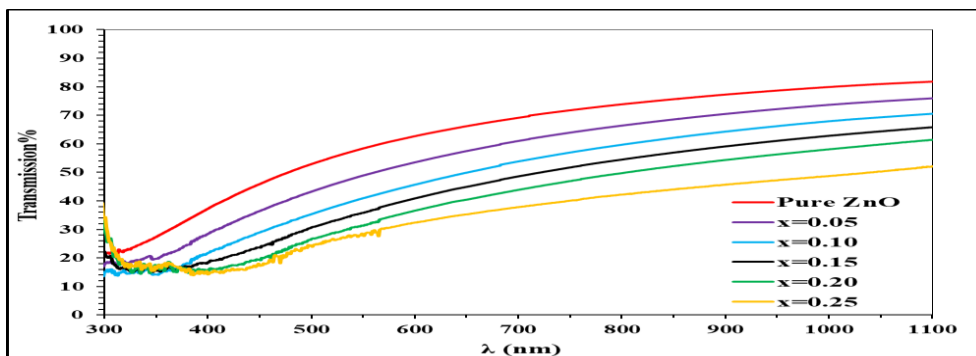
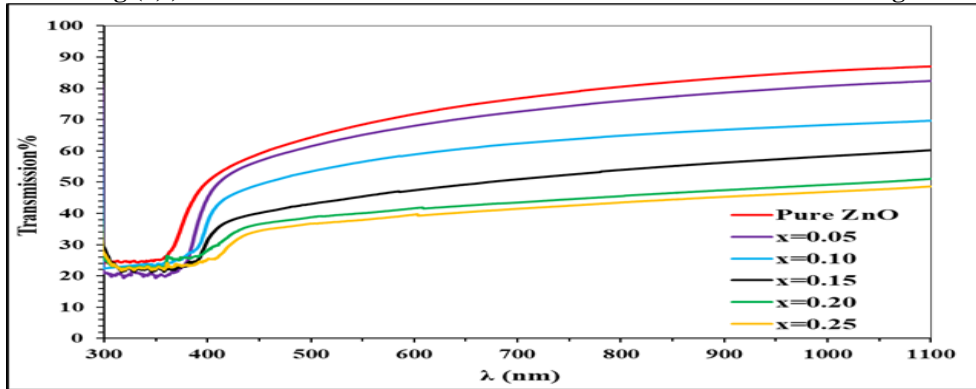**Fig (3))Transmission for Zn2SiO4 with different ratio before annealing**

Fig (4))Trancmission for Zn$_2$SiO$_4$ with different ratio after annealing

3-3-Absorption coefficient

The absorption coefficient, which is denoted by the symbol α, is defined as the percentage of the decrease in the energy of the radiation relative to the unit of distance towards the propagation of the wave within the center and the absorption coefficient of the relationship was calculated [10].

$$\alpha = 2.303 \, A / t \ \text{------- (1)}$$

Where α -Absorption coefficient,A- absorption and t-Thickness .

Fig(5) and (6) declare that the doping resulted in an increase in the absorption coefficient due to the generation of secondary levels within the energy gap near the conduction band, which increased the probability of low photon absorption. After the annealing we notice a decrease in the absorption coefficient due to crystallization of the material, which reduced the crystalline defects resulting from a defect in the stacking or defect in the crystal structure. this results agree with references [11].
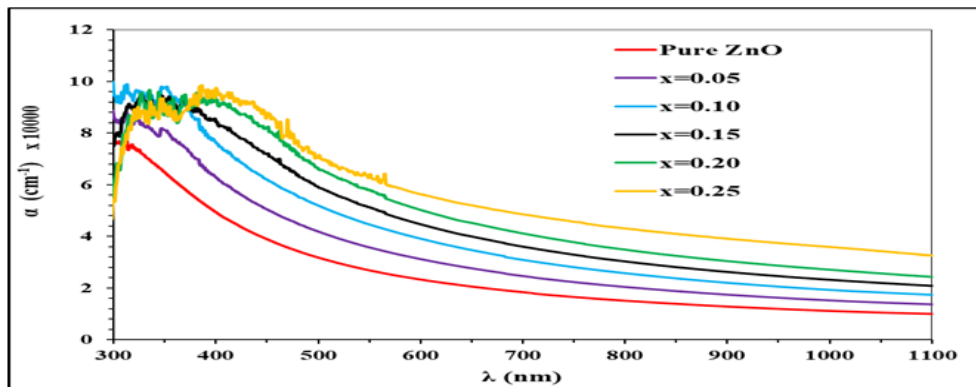

Fig (5))Absortance coefficient for Zn$_2$SiO$_4$ with different ratio before annealing
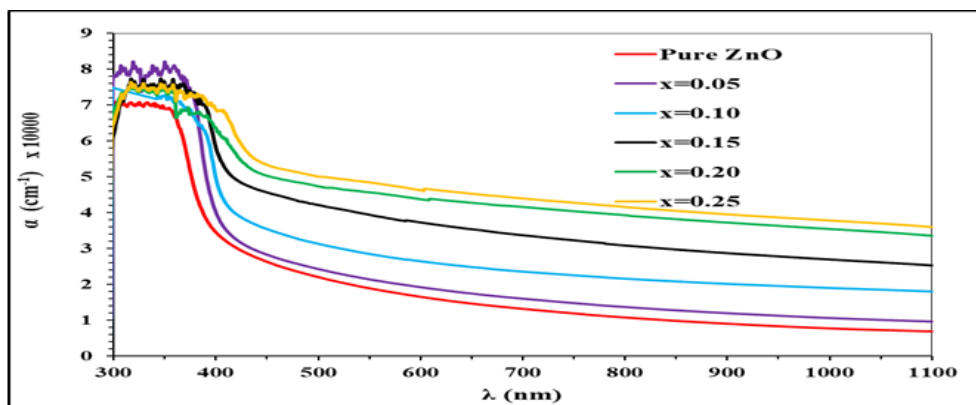

Fig (6))Absortance coefficient for Zn2SiO4 with different ratio after annealing

3-1-4 - Energy gap

It is known as the energy needed to transfer an electron from the top of the valence band to the bottom of the conduction band . It is one of the most important optical constants that rely on semiconductor physics to manufacture many

electronic devices. The value of the energy gap was calculated using the relationship [12].

$$(\alpha h\nu) = B \, (h\nu - E_g)^r \ \text{--------(2)}$$

Where: α-absorption coefficient, ν energy photon, B constant, Eg energy gap, r exponential amount and r value is ½ because its direct transition. And by

quadrature the equation, we get the following equation

$$(\alpha h\nu)^2 = B^2 (h\nu - E_g) \quad \text{--------(3)}$$

Fig (7),(8) show that the doping leads to a decrease in the energy gap values with increased doping rates. Increasing the doping rate leads to new topical levels below the conduction band. These levels are ready to

receive electrons and generate tails in the optical power gap. These tails work toward reducing the energy gap. Annealing lead to decreased levels of localized near valence band (decrease tails in the optical energy gap) as a result of crystallinety enhancement cause to increase the optical band gap . This results agree with references [13-17].
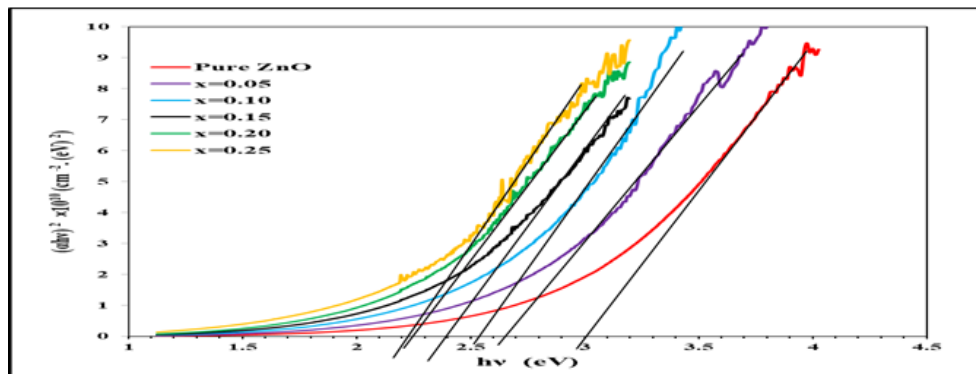

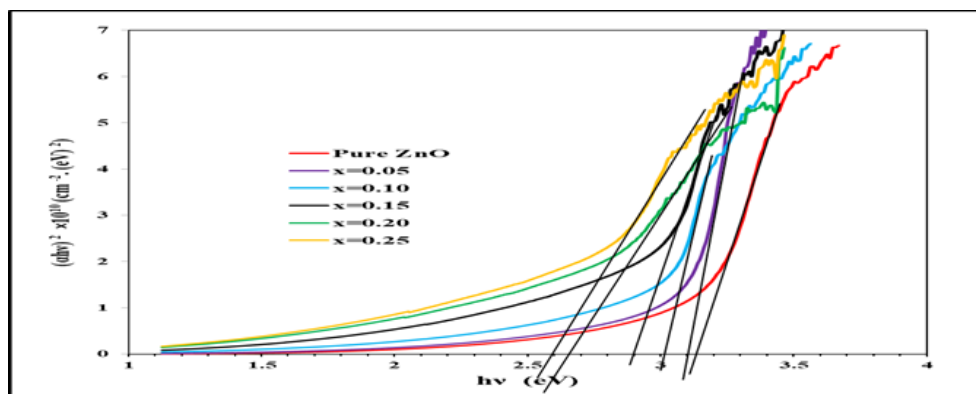**Fig (7))Energy gap for Zn$_2$SiO$_4$ with different ratio before annealing**

Fig (8))Energy gap for Zn$_2$SiO$_4$ with different ratio after annealing

4- Conclusion

1- Annealing led Increased absorption and decreased transmission because crystallization of the material which in turn led to reduce crystalline defects.
- Absorption increases by increasing doping rates. 2

3-The Transmission is reduced by an increase of the doping rates

4-Absorption coefficient increases from(8-10) cm^{-1} before annealing and from (6-8) after annealing .

5- The energy gap decrease from (3) eV to(2.2) eV before annealing and after annealing decrease from (3.15) eV to(2.6) eV by increase ratio of dopping.

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تأثير التشويب بأوكسيد السيليكون على الخواص البصرية للأغشية أوكسيد الخارصين الرقيقة المحضرة بتقنية الترسيب بالليزر النبضي

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الملخص

في هذا البحث تم تشويب اوكسيد الخارصين بنسب تراكيز (25,20,15,10,5) % من اوكسيد السيليكون ورسب الخليط على ارضيات زجاجية بتقنية الترسيب بالليزر النبضي وفي درجة حرارة الغرفة للحصول على اغشية سليكات الخارصين. تمت دراسة الخواص البصرية للاغشية المحضرة من خلال طيف الامتصاصية والنفاذية ضمن مدى الاطوال الموجية nm (200-1000). تم حساب بعض الخواص البصرية ومنها الامتصاصية والنفاذية ومعامل الامتصاص وفجوة الطاقة قبل وبعد التلدين لمدة ساعة واحدة وبدرجة حرارة (400C°). أظهرت النتائج زيادة في الامتصاصية ومعامل الامتصاص بعد التشويب ونقصان النفاذية وفجوة الطاقة بعد التشويب. أظهرت النتائج نقصان الامتصاصية ومعامل الامتصاص بعد التلدين وزيادة النفاذية وفجوة الطاقة بعد التلدين.