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Synthesis Characterization and Optical Properties of Nanostructured Zinc Sulfide Thin Films Obtained by Spray Pyrolysis Deposition

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Abstract: In this work, nanostructure zinc sulfide (ZnS) thin films at temperature of substrate 450 ^oC and thickness (120) nm have been produced by chemical spray pyrolysis method. The X-Ray Diffraction (XRD) measurements of the film showed that they have a polycrystalline structure and possessed a hexagonal phase with strong crystalline orientation of (103). The grain size was measured using scanning electron microscope (SEM) which was approximately equal to 80 nm. The linear optical measurements showed that ZnS nanostructure has direct energy gap. Nonlinear optical properties experiments were performed using Q-switched 532 nm Nd:YAG laser Z-scan system. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) estimated for ZnS nanostructure for different intensities of laser beam. It has been found that n_2 and β were decreased with increasing of intensity of incident laser beam. Also, two photon absorption has been observed. The first type of n_2 was positive nonlinear reflective index and the second type of n_2 was self-focusing nonlinear refractive index for the sample.

Introduction

ZnS nano particles could be used as good photo catalysts due to rapid generation of the electron -hole pairs by photo excitation and highly negative reduction potentials of excited electrons;

As conduction band position of ZnS in aqueous solution is higher than that of other semiconductors such as TiO_2 and ZnO [1]. Since a higher ratio of surface to volume of a catalyst would facilitate a better catalytic activity, the size controlled synthesis of ZnS nanostructures to produce a high surface to volume ratio is of great importance.

The enhanced surface to volume ratio causes an increase of the surface states, which change the activity of electrons [2].

The optical properties of a semiconductor can be defined as any property that involves the interaction between electromagnetic radiation or light and the semiconductor, including absorption, diffraction, polarization, reflection, and scattering effects….etc [3].

The high intensity of the laser beam causes nonlinear optical processes, in which the optical parameters of the material, such as the absorption coefficient, the refractive index, will be affected. The term nonlinear is derived from the expression for the polarization of the material P induced by the electric fields E associated with the optical beams [4].

The aim of present work is to prepare a nanostructure ZnS thin film by chemical spray pyrolysis method and studies the structure and the linear and nonlinear optical properties of it.

Experimental work

Sample preparation

Thin films of nanostructure ZnS were prepared using zinc acetate and thiourea as precursors. The concentration of solution was 0.05 M .The nanostructure ZnS films was formed at temperature of the substrate of (400) °C. Square glass sheet with (2.5×2.5) cm^2 area of 1mm thickness was used as a substrate.The substrate should be cleaned very well before the beginning of the spray operation. The spraying operation was continued for several times. Then, the layers appeared on the surface of the substrate. The film thickness deposited at temperature of (400) ^{o}C was (200) nm.

Measurements

After preparing the ZnS thin film, the structure measurement, linear optical properties measurement, and nonlinear optical properties measurement have been done. Thin films have been examined by XRD method using model (Shimad Zu 6000- Japan). The nanostructure ZnS thin film was tested using UV-VIS spectrophotometer type (SP3000, Optima, and Japan) for measuring the transmittance (T) and absorbance (A). The linear optical constants, the (refractive index - **n-** as well as the absorption coefficient- α , the Extinction coefficient (K) and Real and Imaginary part of the dielectric constant ε_1 and ε_2) can be found from transmittance spectrum of the films by the following equations[4]:

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

Where A is the absorbance spectrum
t is the thickness of the thin films .
The refractive index is calculated from [5]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad (3)$$

Where R is reflectance and it equal
R=1-(T+A)
The extention coefficient is given by [5]:
K = α λ / 4π (4)
Where λ is the wavelength.
The Real and Imaginary parts of the dielectric constant can be calculated as follows [5]:

$$\varepsilon_1 = n^2 - k^2 \ldots \qquad (5)$$

$$\varepsilon_2 = 2nk \ldots\ldots \qquad (6)$$

Results and Discussions:
X-Ray Measurements:

Figure (1) shows X-ray diffraction pattern of ZnS thin film. This figure of various thin film deposited at 400Co temperature of substrate was shown. It is seen from the XRD patterns that the thin films showed a polycrystalline hexagonal structure with narrow peaks indicating a large grain size. The analysis is demonstrated the reflection surfaces at (101),(102), (103),(006) and (110) . All patterns reveal a strong peak at (103) directions, which corresponds to typical (covellite) with lattice constant of a=3.792 A° and c=16.344 A°. This means that this plane is suitable for crystal growth.

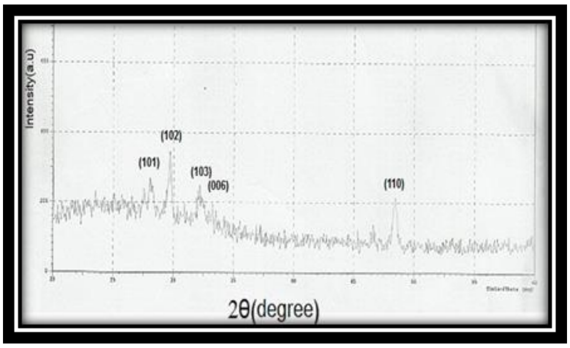

Fig.(1): X-ray diffraction pattern of ZnS thin film

Linear optical properties:

Thin film is not highly transparent in the visible region of the electromagnetic spectrum .The maximum value of the transmittance is about (49.5%) recorded for film with thickness (200 nm), Figure (2) shows the variation of (α) with photon energy for ZnS thin film .

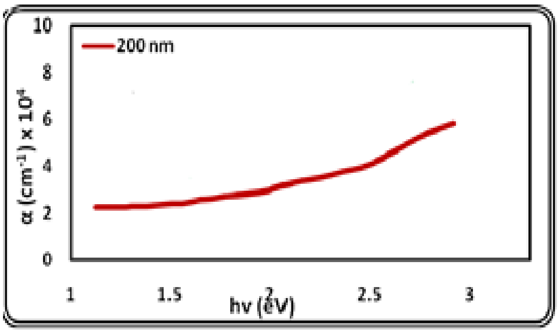

Fig. (2): Absorption coefficient as function of energy photon for nanostructure ZnS thin film

From this figure, it can be seen that the absorption coefficient (α) increases with increasing photon energy for investigated thin films. It can evidently be seen that the absorption coefficient having values (which leads to increase the probability of occurrence direct transition. Also, the extinction coefficient as a function of λ takes the same behavior of α as a function of hυ (eV) according to eq.(4). Figure (3) show the direct energy gap for nano ZnS thin films .

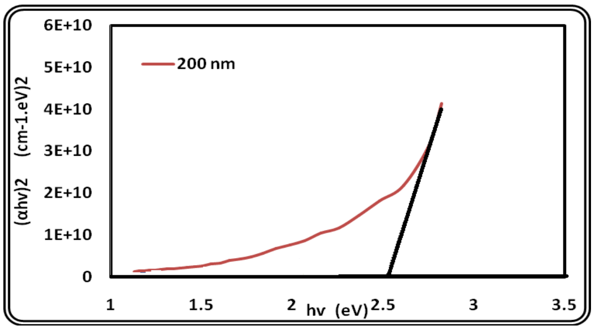

Fig. (3): $(\alpha h\nu)^2$ as function of energy photon for nanostructure ZnS thin film

$$\alpha h\nu = B\left(h\nu - E_g^{\ opt.}\right)^{\frac{1}{2}} \qquad (7)$$

The coefficient B (taus slope) in the equation (7) has been obtained from the values of Eg and B is tabulated in the table (1). We Know that B is proportional inversely with randomness of amorphousity structure and the width of the band tails, a larger B value means a smaller randomness.

$$\alpha(\nu) = \alpha_o \exp\left(\frac{h\nu}{E_u}\right) \qquad (8)$$

Below $\alpha \approx 10^4$ (cm)$^{-1}$ there is an absorption tails at energies smaller than optical energy gap which is called Urback energy (E_u) and the absorption coefficient exhibits an exponential behavior. Equation (8) gives the value of E_u. The Urbach energy gives information about localized state in the band gap and its values tabulated in table (1). This effect can be explained by increasing in packing density because of decreasing the degree of amorphousity of films leads to decrease in localized state.

Table (1): Optical parameters Eg , B and Eu for ZnS thin film**.**

thickness (nm)	E_g eV	Bx10^4 eV$^{1/2}$ cm^{-1}	E_u eV^{-1}. Cm^{-1}
200	2.5	5	1.4

Nonlinear Optical Properties:

The nonlinear optical properties were measured for nano ZnS thin films at 200 nm and 400 c temperature of substrate. Different intensities (1.63, 2.44 and 3.26) GW/cm^2 were used Q-switched Nd:YAG laser 532nm respectively.

Nonlinear Refractive Index:

For closed Z-scan ZnS thin films for different intensities we can observe the positive nonlinear refractive index. Figures (4-a,b) shows that all film behaviors were self-focus NLR, the nonlinear refractive index is equal to 1.4*10^{-2} cm^2/GW.

The quantum confinement effects as well as the large surface to volume ratio for quantum dots having smaller size have caused the enhancement in the nonlinearity , also in quantum dots the absorption is determined by the confined transition , however, that for the refractive index a large numbers, And we see the same behavior for all intensities[4].

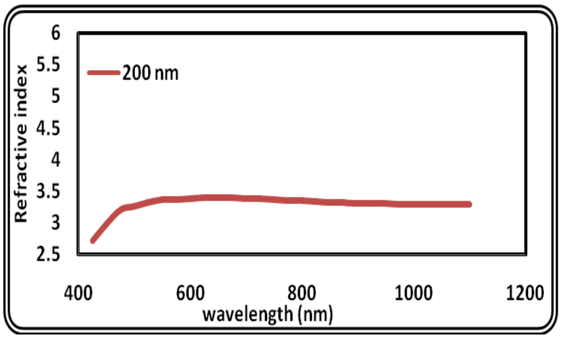

Fig. (4-a): Refractive index as function of wavelength for different thickness of nanostructure ZnS thin films.

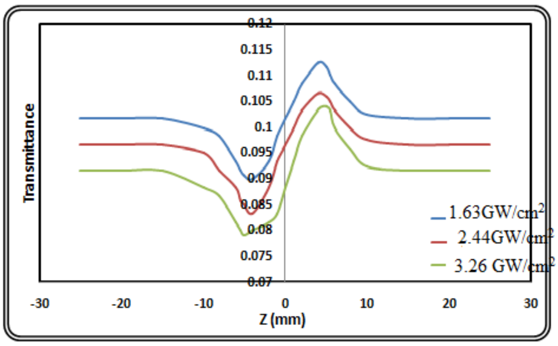

Fig. (4-b): Closed-aperture of nanostructure ZnS thin film at 200 nm thickness for (1.63, 2.44 and 3.26) GW/cm^2 at 532 nm

Nonlinear Absorption Coefficient:

The nonlinear absorption coefficients β of ZnS thin films were measured by performing the open aperture z-Scan technique. β is related to the imaginary part of the third-order optical susceptibility $\chi^{(3)}$.Open aperture-Scan that performed in this study exhibited a reduction in the transmission about the focus of the lens.

The transmittance curves of ZnS thin films at different intensities at 532 nm are shown in Figure (5). The behavior of transmittance started linearly at different distances from the far field of the sample position (-Z). The nonlinear absorption coefficient is equal to 122 cm/GW.

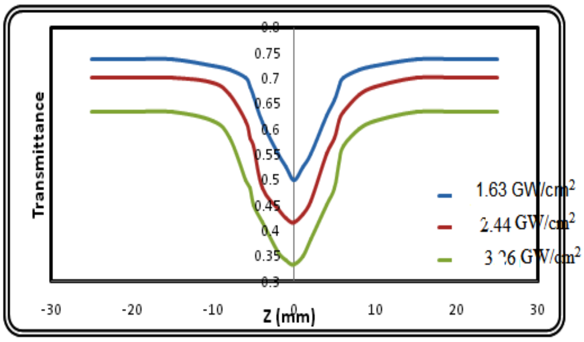

Fig. (5): Open-aperture of nanostructure ZnS thin film at 200 nm thickness for (1.63, 2.44 and 3.26) GW/cm^2 at 532 nm.

At the near field the transmittance curve begins to decrease until it reaches the minimum value (T_{min}) at the focal point, where Z=0 mm. The transmittance begins to increase toward the linear behavior at the far field of the sample position (+Z).

The incident photon energy of laser at λ=532 nm, E=1.165 eV .Also the energy gap of thin films 200nm , was 2.6 eV. Thus the condition 1E<Eg<2E .It clearly the possibility of occurrence of two photon absorption (2PA) and three photon absorption (3PA) are operative and dominant mechanism for present experimental observations[4,6] .

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تحضير ودراسة الخواص الضوئية لغشاء رقيق من جزيئات كبريتيد الزنك النانومترية والمحضرة بطريقة الرش بالترسيب الحراري

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الخلاصة في الدراسة الحالية تم تحضير غشاء رقيق من كبريتيد الزنك عند 450 درجة مئوية للمادة الاساس وبسمك مقداره 120 نانومتر بطريقة الرش بالتحلل الحراري الكيميائي . بينت قياسات حيود الاشعة السينية ان الغشاء المحضر هو ذا تركيب بلوري سداسي الطور وبأتجاه (103) وبحجم بلوري مقداره 20 نانومتر والذي وجد بأستخدام مجهر المسح الالكتروني . كذلك اثبتت الفحوصات الضوئية الخطية التي اجريت انه الاغشية المحضرة تمتلك فجوة الطاقة. وكذلك اجريت بعض الفحوصات الضوئية اللاخطية بأستخدام ليزر النديميوم – ياك عند 532 نانومتر بتقنية المسح على المحور الثالث . معامل الانكسار اللاخطي ومعامل الامتصاص اللاخطي تم حسابه عند شدات مختلفة لليزر. وقد وجد معامل الامتصاص اللاخطي (امتصاص ثنائي الفوتون).ومعامل الانكسار اللاخطي موجب.