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Nonlinear Optical Properties of CdS Thin Film Nanoparticles Using z-Scan Technique

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Abstract: In the present work, a z-scan technique was used to study the nonlinear optical properties, represented by the nonlinear refractive index and nonlinear absorption coefficients of nanoparticles cadmium sulfide thin film. The sample was prepared by the chemical bath deposition method. Several testing were done including, x-ray, transmission and thickness of thin film. z-Scan experiment was performed at two wavelengths (1064 nm and 532 nm) and different energies. The results showed the effect of self-focusing in the material at higher intensities, which evaluated n_2 to be (0.11-0.16) cm^2/GW. The effect of two-photon absorption was studied, which evaluated β to be (24-106) cm/GW. In addition, the optical limiting behavior has been studied. The results confirmed the capability of the sample to be used as optical limiter device.

Introduction

Nanostructure materials (NSM) are new type of materials that exhibit unique features and properties in different fields. They exhibit wide variety of nonlinear optical properties, which have attracted attention of the nonlinear optical devices [1,2]. Nanoparticles CdS thin film has many applications in piezoelectric, laser materials, photovoltaic cells, solar cells and optoelectronic devices [3,4]. Several techniques were used to synthesis the nanostructure materials including, the chemical bath deposition (CBD) that is attractive as a simple and low cost method.

The process of thin film deposition involves the deposition of material atom-by-atom, molecule-by-molecule, or ion-by-ion and cluster by cluster. This method is applied extensively in the manufacture of photocells, optical coating and microelectronics. The technique of chemically depositing thin films has the advantage of being a low cost and applicable to the production of large-area devices [5-7].

The interests in the nonlinear optical properties of nanometer-sized semiconductors have become a subject of intensive research for their extraordinary properties compared to their bulk counterparts [8]. Wide ranges of techniques have been used to measure nonlinear optical properties such as, z-scan technique [9,10].

In 1989 M. Sheik-Bahae et al.[11] reported the z-scan technique for measuring both the nonlinear refractive index and nonlinear absorption coeffiecint for a wide varity of materials. z-Scan method provides a straightforward method for the determination of the nonlinear refractive index and the nonlinear absorption coefficient. The simplicity of both the experimental set-up and the data analysis has allowed the technique to become widely used by research groups [11].

The aim of this work was the use of the z-scan technique to study the nonlinear properties of cadmium sulfide thin film nanoparticles. Also preparing a good limiter device for many applications

Theory

There is considerable interest in finding materials having fast nonlinearities. This interest, that is driven primarily by the search for materials for all-optical switching and sensor protection applications, concerns both nonlinear absorption (NLA) and nonlinear refraction (NLR). The absorption of the material at high intensity is given by [12]

$$\alpha = \alpha_o + \beta I \qquad (1)$$

where α_o is the linear absorption coefficient and β is the nonlinear absorption coefficient related to the intensity. At high intensity, the refractive index is given by [11,12]

$$n = n_o + n_2 I \qquad (2)$$

where n_o is the linear refractive index, n_2 is the nonlinear refractive coefficient related to the fluence. The nonlinear optical properties can be investigated by z-scan technique at which it can be used to determine the nonlinear refractive index when closed-aperture geometry is used, and nonlinear absorption coefficient with open-aperture.

The nonlinear refractive index is calculated from the peak to valley difference of the normalized transmittance by the following formula [11]

$$n_2 = \Delta\Phi o / I_o L_{eff}\, k \qquad (3)$$

where $\Delta\Phi o$ is the nonlinear phase shift, $k = 2\pi/\lambda$, λ is the beam wavelength, I_o is the intensity at the focal spot, L_{eff} is the effective length of the sample, determined from [11]

$$L_{eff} = (1-e^{-\alpha o L}) / \alpha_o \qquad (4)$$

where L is the sample length, α_o is linear absorption coefficient.

The intensity at the focal spot is given by [13]

$$I_o = 2P_{peak} / \pi\omega_o^2 \qquad (5)$$

where ω_o is the beam radius at the focal point, P_{peak} is the peak power given by [13]

$$P_{peak} = E / \Delta t \qquad (6)$$

where E is the energy of the pulse, Δt is the pulse duration.

The coefficients of nonlinear absorption can be easily calculated from such transmittance curves. The total transmittance is given by [11]

$$T(z) = \sum_{m=0}^{\infty} \frac{\left[\dfrac{bI_o L_{eff}}{1+(z/zo)^2}\right]^m}{(m+1)^{3/2}} \qquad (7)$$

where z is the sample position at the minimum transmittance, z_o is the diffraction length, m is an integer, and $T(z)$ is the minimum transmittance.

Experimental

Sample Preparation

Nanoparticles CdS films were prepared from cadmium sulfate and thiourea by chemical bath deposition in alkaline solution.

Different bath concentrations were used in different composition as shown in Table (1). The deposition of CdS films was achieved from dilute solutions. Sulphide ions are released in the bath by the hydrolysis of thiourea, in the presence of OH^- ions. Cd^{2+} ions are complexed with one or more of the complex agents like NH_3 [directly added as NH_3 (aq)], or NH_4C1. This ensures slow release of Cd^{2+} ions in the solution [5-7].

The homogeneity of grain growth and the uniform distribution of the nanoparticles can be adjusted by applying the uniform temperatures with a better reaction chamber.

Table (1) concentration of the reactants compounds

Chemical Compound	Formula	Concentration -M-	pH	Volume -ml-
Cadmium Sulfate	$CdSO_4$	0.015	8.3	2
Thiourea	$CS(NH_2)_2$	1.5	8.5	2
Ammonium Hydroxide	NH_4OH	14.3	9	3

Sample Testing

X-ray diffraction (XRD) test

PW 1840 diffractometer equipped with radiation source (40 kV, 20mA) and λ = 0.154 nm was used. The average size of particles was calculated from XRD peak broadening using Scherer formula [14]. The x-ray diffraction pattern of CdS is shown in Fig.(1).

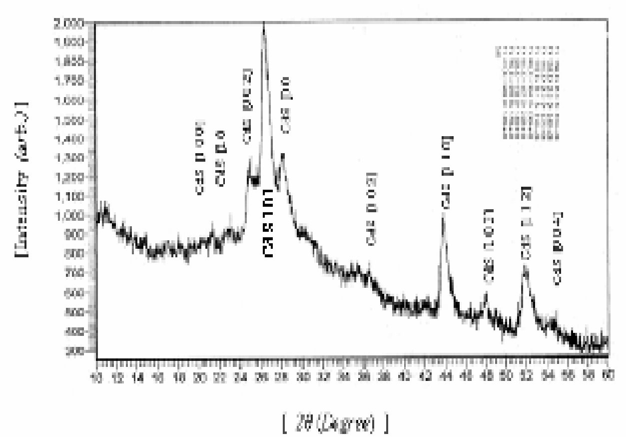


Fig. (1) X-ray diffraction pattern of CdS film growth

Transmission testing

The sample was tested using UV-visible spectrophotometer for measuring transmission spectra of CdS film and substrate. Fig. (2) shows the transmission spectra of the CdS thin film and the substrate.

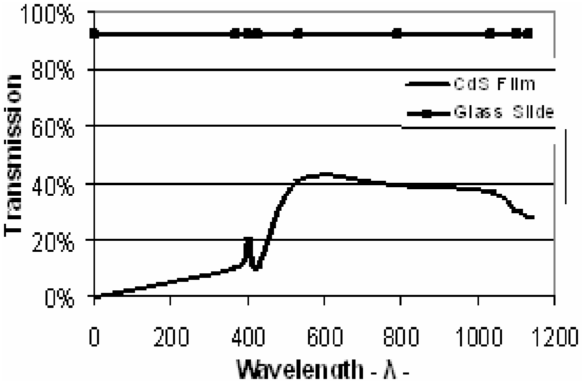
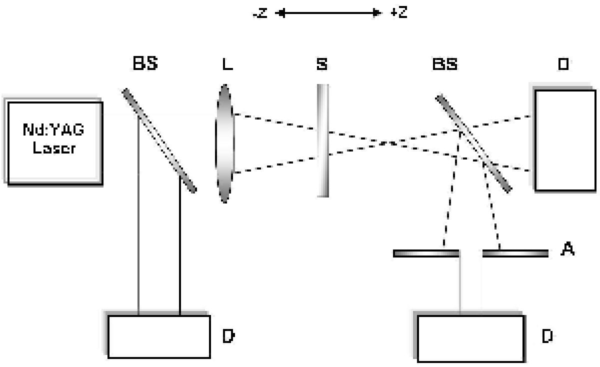


Fig. (2) The optical transmission of CdS deposited onto glass substrate

z-Scan System

Closed and open aperture z-scan measurements were done. Each part was employed at 1064 nm and 532 nm. Fig. (3) shows the set-up of the z-scan system.



BS: beam splitter L: Lens S: Sample D: Detector, A: Aperture

Fig. (3) The set-up of z-scan system

Results and Discussion

CdS Film Properties

The precipitation reactions and the homogeneity of the distributed nanoparticles are affected by the environmental conditions and by the applied temperatures. As a result, the most appropriate temperature to start the reaction is 65°C at 3.4 min, because above and below this temperature lead to size dispersion, surface defect, impurity contents, crystallite interface, which in turn limit the optical properties of CdS nanoparticles.

XRD of the CdS nanocrystals reveals diffraction peaks corresponding to the hexagonal structure form. The maximum peak occurred at 26.3°, which arises from the close packing of the individual clusters defining a characteristic equal to the average diameter of the nanoparticles, the average sizes of the nanoparticles were 8 nm.

Transmission spectra at lower wavelength shows that the transmission is limited by the absorption in the in the CdS film. The behavior of the transmission curve is similar to that reported by Grecu [3]. Nonlinear refractive index and nonlinear absorption coefficients were obtained at 1064 nm and 532.

Nonlinear Refractive Index

In order to investigate the nonlinear refractive index, two cases were chosen at 1064 nm and 532 nm. At case I, Fig. (4) shows the closed-aperture z-scan results at 1064 nm at different intensities of the laser source.

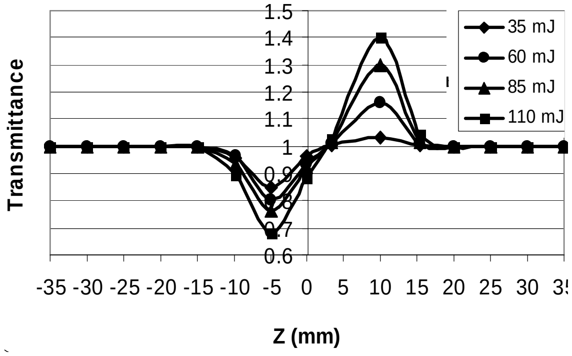


Fig. (4): Closed-aperture z-scan at 1064 nm

At case II, Fig. (5) shows the closed-aperture z-scan at 532 nm at different intensities. The value of transmittance at 532 nm is larger than 1064 nm for the same energy because the energy of photon is larger in 532 nm than 1064 nm.

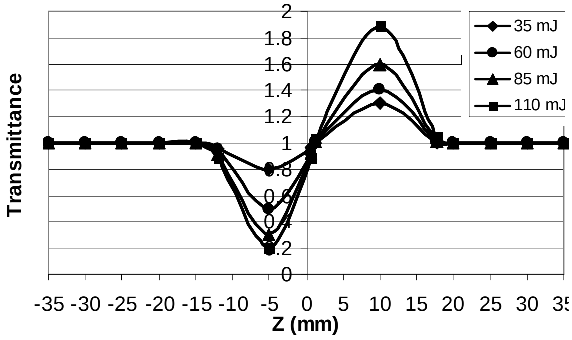


Fig. (5): Closed-aperture z-Scan at 532 nm

A valley followed by a peak is the hallmark of a positive n_2. The peak to valley profile displayed in the figures, demonstrates the sample exhibited a self-focusing effect, i.e., it has a positive nonlinearity at 1064 nm and at 532 nm. The external self-focusing arising from the Kerr effect in CdS, which appears in the peak and valley transmittance of each of z-scan trace.

The magnitude of n_2 depends on the wavelength, but this dependence is not very strong at low pulse energy. The closed-aperture z-scan defines variable transmittance values, which used to determine the nonlinear phase shift $\Delta\Phi$ and the nonlinear refractive index using equation (3).

In addition, the behavior of n_2 can be investigated from Fig. (6) at different fluencies. The variation of n_2 is directly proportional to the input fluence; this variation may arise from such contributions as self-focusing of a sample. The nature of the nonlinear response can be inferred from its dependence on fluence.

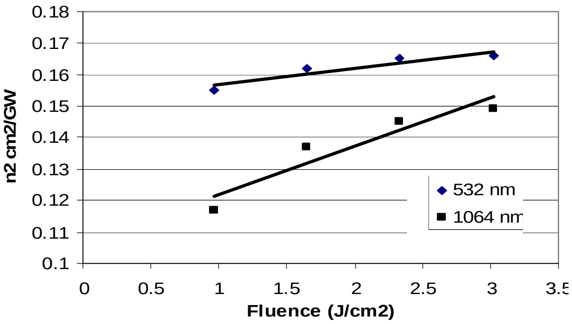


Fig. (6): Variation of nonlinear refractive index versus fluency

Nonlinear Absorption Coefficient

In order to investigate the nonlinear absorption coefficient, two wavelengths were considered 1064 nm and 532 nm. At case I, Fig. (7) shows the open-aperture z-scan at 1064 nm at different energies. At case II, Fig. (8) shows the open-aperture z-scan at 532 nm at different energies. The transmittance is sensitive to the nonlinear absorption as a function of input intensities.

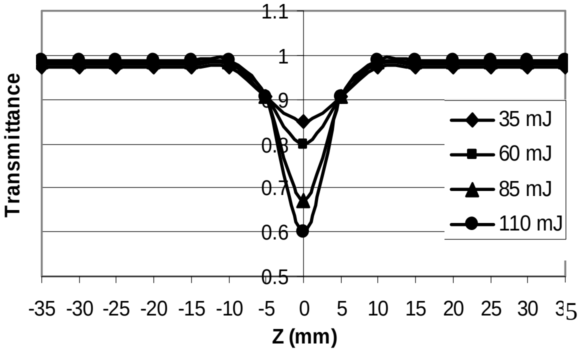


Fig. (7): Open-aperture z-scan at 1064 nm

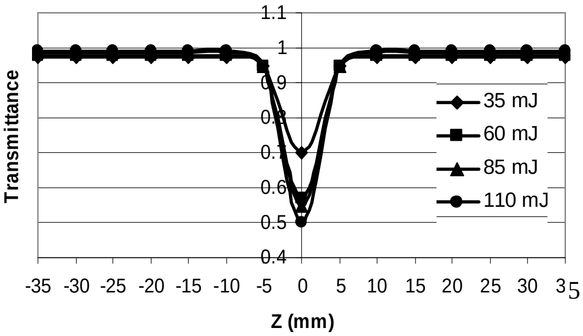


Fig. (8) Open-aperture z-scan at 532 nm

The change in transmittance is caused by two-photon absorption in the sample as it travels through the beam waist [15]. A symmetric valley is contributed to the positive nonlinear absorption coefficient β, indicating the two-photon absorption; this property is more enhanced at 532 nm.

The open-aperture z-scan defines variable transmittance values, which used to determine absorption coefficient. The value of β is decreased by the intensity increased. This behavior can be investigated from Fig. (9).

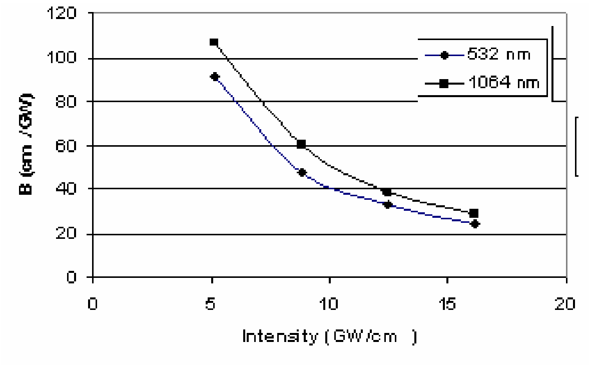


Fig. (9) Variation of nonlinear absorption coefficient versus intensity

The magnitude of β started with larger values at low input intensity, at higher intensities the value of β was decreased very strongly. As the intensity increase there is a significant decreasing in the nonlinear coefficient. Since the CdS film exhibits the two-photon absorption as a function of the input intensity.

Optical Limiting Behavior

At 1064 nm, the limiting behavior was investigated by the z-scan as shown in Fig. (10), the same behavior can be investigated at 532 nm as shown in Fig. (11).

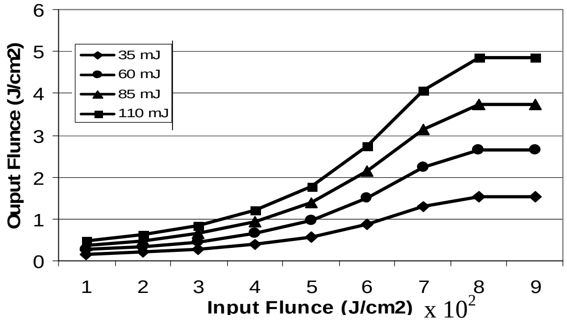


Fig. (10) Optical limiting behavior at 1064 nm

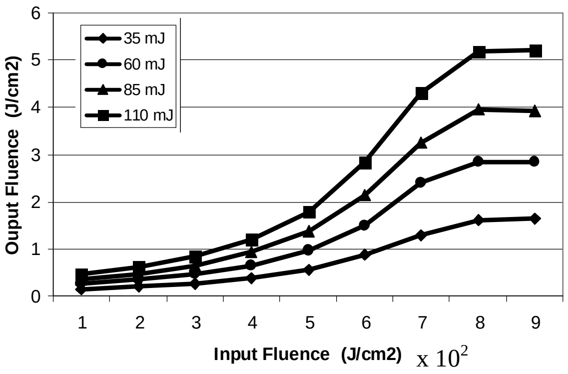


Fig. (11) Optical limiting behaviour at 532 nm

The resulting data from the closed and open-aperture z-scan at the two wavelengths showed a linear behavior for low input fluence much less than the limiting energy, the limiting occurs at approximately, 800 J/cm^2, over which the sample may be damage.

As a result, the nonlinear absorption combined with nonlinear refraction keeps the fluence within the semiconductor below the damage threshold, and the device is self-protected. Since, the larger nonlinearities can actually be used to prevent damage [16].

Conclusions

The numerical investigation demonstrates that the nonlinear optical properties of CdS nanoparticles are more enhanced at 532 nm with the same results but at less effect at 1064 nm. The optical limiting behavior shows that the nanoparticles CdS are the better semiconductor limiters for a wide input fluency without getting damage.

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الخواص البصرية اللاخطية لغشاء رقيق من كبريتيد الكادميوم ذات الجزيئات النانومترية باستخدام تقانة المسح على المحور الثالث

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الخلاصة

في هذا البحث ، استخدمت تقنية المسح على المحور الثالث (z-scan) لدراسة الخواص البصرية اللاخطية مثل معاملات الانكسار والامتصاص اللاخطية لطبقة رقيقة من كبريتيد الكادميوم (CdS) ذات الجزيئات النانومترية والمترسبة على شريحة زجاجية . تم تحضير العينة باستخدام طريقة الترسيب الكيميائي الحراري ، ولغرض التعرف على خصائص العينة تم أجراء عدة فحوصات مختبرية مثل الفحص بالاشعة السينية بالاضافة الى اجراء الفحوصات البصرية الاخرى مثل فحص النفاذية والسمك . تم اجراء تجربة المسح على المحور الثالث بطولين موجيين عند 1064 نانومتر و 532 نانومتر وبطاقات مختلفة. حيث بينت تأثير ظاهرة التبؤر الذاتي للمادة عند الطاقات العالية، حيث تراوحت قيم معامل الانكسار اللاخطي ما بين (0.11- 0.16) كيكاواط / سم^2 . أضافة لذلك تمت دراسة تأثير عملية الامتصاص الثنائي او المتعدد الفوتون للمادة حيث تراوحت قيم معامل الامتصاص اللاخطي ما بين (24-106) كيكاواط / سم^2 . ومن ناحية أخرى فقد تمت دراسة خواص العينة كمحددات بصرية ولوحظ من خلال المخططات الناتجة أمكانية عملها كمحدد بصري ولمدى واسع من الطاقات الداخلة دون حدوث تلف في العينة .