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INVESTIGATING THE NONLINEAR OPTICAL PROPERTIES OF CuS THIN FILMS PREPARED BY CHEMICAL BATH DEPOSITION USING Z-SCAN TECHNIQUE

S. A. HUSSAIN, A. S. HADI, F. A. NAJIM*
Department of Physics, College of Education, University of Al-Qadisiyah, 58002, Iraq

CuS thin films were participated onto glass substrate by using chemical Bath Deposition method at (75°C) for (1hr) with different concentrations (0.03,0.05 and 0.08)M of Thiourea (TU) and Copper Chloride with molar ratio (0.01) have been used for solution preparation. As deposition and annealed films were studied. Non-linear absorption coefficient is measured by using Z-Scan technology and it consists of two sections. The first section is closed opening were located before detector to calculate the non-linear refractive index. Whereas the second section, were aperture located before the detector (the open aperture) is taken to calculate the non-linear absorption coefficient. Both cases are done with a CW laser with a wavelength of 650 nm and a power of 50 MW.

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1. Introduction

Copper sulfide (CuS) is one of the most significant semiconductor materials and it has faced great attention due to its unique chemical and physical properties [1]. It's found in various types of phases as Dignity ($Cu_{1.8}S$), Anilite ($Cu_{1.75}S$), Djurleite ($Cu_{1.95}S$), and Covellite (CuS) that shows one of the important materials because of their chemical and physical properties and it has become a significant contender for using in the industrializing solar cells [2]. Many methods can be used to prepare thin films such as chemical bath deposition, electrodeposition method, vacuum evaporation [3,4,5]. The chemical processes are so eligible and economical. Therefore, the development of CuS thin films can make it with desirable structure [4]. CuS thin films properties are affected by a precise chemical measurement, which based on preparation conditions for thin film deposition. CuS thin films have gotten a lot of consideration due to their different technological purposes that applied in photovoltaic applications such as Cu_2S / CdS solar cells that have shown about 10% of efficiency [6]. Chalcocite (Cu_2S) is one of the active layer especially in film such as $Cd_{1-y}Z_{ny}S$/ Cu_2S cell [7]. Solar photoelectric conversion (as a coating for solar absorption) as in filters that used for selecting the wave length of radiation on architectural windows (for controlling the warm environment in conductive electroplating) were deposited on an organic material (polymers). The important features were obtained by using Cu_xS as sensing applications at low operating temperature [8]. In this work we used Z-scan technique to study non-linear characterizations of CuS thin films prepared with 75°C and deposited on glass layer were annealing temperature at 120°C for 2hrs.

2. Experimental details

In 1990 M.SheikBaha was established the technique of refractive nonlinear fine samples[9]. This technique is called scanning technique Z [10]. The Fig. 1 shows the basic geometric form.

* Corresponding author: firas.najim@qu.edu.iq

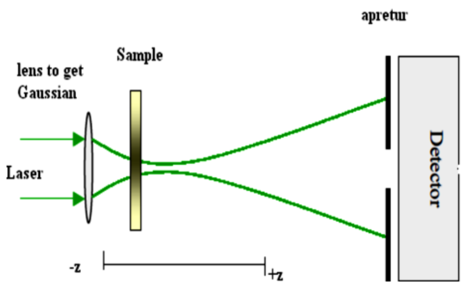

Fig. 1. Arrangement of Z-scan experiment [11].

Along the Z- direction the sample is scanning according to z-scan technology via focus of the center by Gaussian beam of laser with a narrow focus formation, as shown in figure 1. The sample approaches to the focus, the laser spot size will decreases, that will increase radiation of the sample and that will generate non-linear influences [12]. There are two modes of the Z scan: a closed and an open aperture and the closed aperture is an incident self-refraction occurring in the projected beam or self-phase modification. In the case of induced non-linear absorption, the peak and the valley are functional. Fig. 2 shows closed aperture geometry.

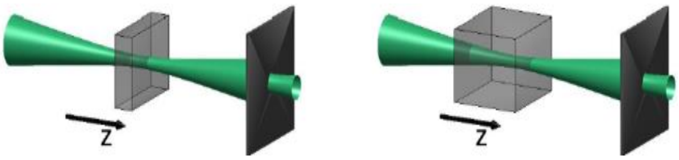

Fig. 2. Closed aperture geometry [13].

Non-linear refractive index can be specified by noticing the variation in transmittance via a narrow circular aperture that was placed at the location away. The samples are moved in regular steps are equals to 1 mm during the scanning process [14]. When the specimen are moved along z-axis in relation to the contact point, the relationship between transmittance (T) and the location in z- axis can be achieved. We define an easily determinate ability ΔT_{p-v} the difference between the transmittance of the valley and its greatest calibrated value (normalized peak). ΔT_{p-v} is found linearly dependent on the induced phase distortion. The deviation quantity with respect to $\Delta\Phi_o$ is given by [15]:

$$\Delta T_{p-v} = 0.406\Delta\Phi_o \tag{1}$$

$$\Delta T_{P-V} = T_P - T_V \tag{2}$$

$\Delta\Phi_o$the temporally averaged induced phase distortion

ΔT_{p-v} difference in permeability between valley and peak. Non-linear refraction is given by formula:

$$n_2 = \Delta\Phi_o / I_o L_{eff} k \tag{3}$$

where n_2 = non-linear refractive index

$$k = 2\pi/\lambda \tag{4}$$

$$I_o = 2p/\pi w_o^2 \tag{5}$$

where; λ wavelength of laser beam, I_o intensity of the incident beam at (Z = 0), P power beam , w_o radius of the beam at the focal point.

$$L_{eff} = (1 - exp^{-\alpha_0 t})/\alpha_o \tag{6}$$

(L_{eff}) and (t) effective and thickness of the sample respectively.

The non-linear absorption value of the specimen is clearly appears at aperture Z-scan of open scanning. In the case of non-linear absorption such as two-photon absorption (TPA), this may be represented by measurements with the lowest transmittance at the focal point. Moreover for storable absorbers device, it indicates that the transport increases with the growth of the intensity of the incident and will leads to a better transport in the focal area. The model firstly developed by Bahai and others, for pure TPA it can used to excited absorption condition [16]. Fig. 3 shows an open aperture geometry.

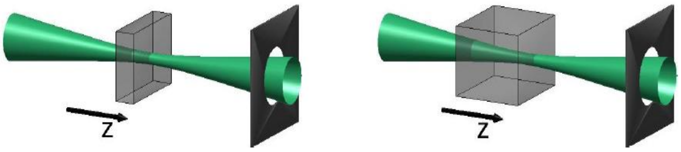

Fig. 3. Open aperture geometry.

Non-linear absorption coefficients calculated from curves of transmittance using equation (7) [11]:

$$\beta = \frac{2\sqrt{2}}{I_0\, L_{eff}} T \tag{7}$$

where T represent the peak value at open aperture curve, β is the non-linear absorption coefficient. β will be in positive values for saturation absorption and in negative values for two-photon absorption [17]. Non-linear optical susceptibility for real and imaginary parts $\chi^{(3)}$ for third order can be determined from experimental observation of n_2 and β due to the following [18]:

$$\mathrm{Re}\,\chi^{(3)} = 10^{-4}\frac{\varepsilon_0 C^2 n_0^2}{\pi} \quad \text{in} \left(\frac{cm^2}{W}\right) \tag{8}$$

$$\mathrm{Im}\,\chi^{(3)} = 10^{-2}\frac{\varepsilon_0 C^2 n_0^2 n_2 \lambda\beta}{4\pi^2} \quad \text{in} \left(\frac{cm^2}{W}\right) \tag{9}$$

c is the velocity of light, $n_\circ$ refractive index .The absolute value was calculated from the following [18]:

$$|\chi^{(3)}| = \left[(Re(\chi^{(3)}))^2 + (Im(\chi^{(3)})^2\right]^{\frac{1}{2}} \tag{10}$$

Many researchers showed that dependence of absorption coefficient (α) and refractive index (n) on the optical properties of intensity of the laser beam [18]. When energy (hυ) is equal to the difference between the energy states, in this case, there is a possibility of photons moves to upper level with consideration that linear absorption (α_0). A non-linear absorption (β) can represent by increased strength of the electric field, it results an increasing of the arrival of absorption photons or multiple photons. Also will investigate changing in refractive index when the electrical field's suspension of the material will increases. The properties of the optical materials are (the coefficient of total absorption and the index of total refraction) depend on the strength of the electric field with a high density which can be given by [19]:

$$n = n_0 + n_2 I \tag{11}$$

$$\alpha = \alpha_0 + \beta I \tag{12}$$

α_0 represent linear absorption coefficient.

Chemical bath deposition method is used because it covers wide area, cheap and wide to use. To prepare the solution, it is used with copper chloride and thiourea to precipitate a thin layer of CuS and to determine the amount of materials required using the formula:

$$M_o = \frac{W_t}{M_{wt}} \times \frac{1000}{V} \tag{13}$$

where M_o represent molar concentration, W_t weight in grams, M_{wt} is the molecular weight for materials in (g / mol) and V distilled water volume (ml).We calculated three weights (0.228,0.380,0.608) gm of TU. Dissolved with (0.1704 g) of copper chlorides in distilled water with 100ml. To prepare thin films, the solution was used to deposit films with (75°C) on glass substrates. The solution was dissolving convenient amounts copper chloride ($CuCl_2.2H_2O$) with 99% purity supplied from German company (Fluka) and Thiourea ($(NH_2)_2CS$ with 99% purity supplied from Spanish company (Sharlve) into distilled water. With molar concentrations of Copper Chloride equal to (0.01m) and Thiourea equal to (0.03, 0.05 and 0.08) M, the PH value of solution equal to (2) by added drops of sodium hydroxide. For good quality for the films, glass substrates were cleaned by using alcohol (methyl ethyl ketone C_4H_8O) (99.9% purity) and then placed in ultrasonic bath full of distilled water for 15minutes and leave them dry in air. Finally using Z-Scan technology with closed and open aperture to measure refractive and absorption coefficient for different concentrations by using diode laser (650nm) with output power (50MW), lens of focal length equal to (30 cm).

3. Results and discussion

Z-scan experiments were done using diode laser of 650 nm with maximum power equal to 50mW max power, with beam diameter of 1.5 mm focused by 30 cm focal length lens. Focus of beam waist ω_o is measured to be 0.015 mm and the results of closed and open aperture z-scan shows in Table1.

Table 1. Results of optical measurements for CuS thin films with different molar concentration

Con. (mol./l)	λ (nm)	ΔT_{P-V}	$I_o \times 10^6$ (mW/cm^2)	$\Delta\phi_o$ (Rad)	$n_2 \times 10^{-13}$ (cm^2/mW)	T_{max}	β (cm/mw) $\times 10^{-7}$
0.03	650	0.451	14.154282	1.11	8.145	1.3	2.6
0.05	650	0.393		0.967	7.093	1.2	2.4
0.08	650	0.398		0.98	7.249	1.13	2.28

From the transmission spectrum the values of refractive index for non-linear CuS thin film were calculated for closed and open aperture as shown in Fig. 4 and it is clear that CuS thin film showed exhibited self-focusing. As shown the refractive index was decreasing with increasing molar concentration of the solution and calculation of the absorption coefficient from the transmission spectrum using open aperture z-scan as shown in Table 1. Fig. 5 showed the results of the non-linear absorption coefficient and saturation absorption of each concentration.

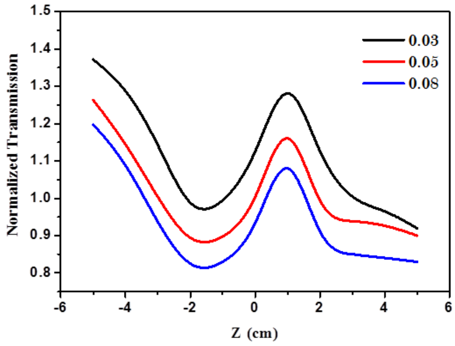

Fig. 4. Experimental data for closed aperture z-scan.

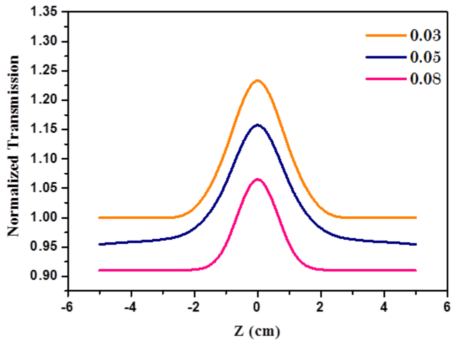

Fig. 5. Experimental data for an Open aperture z-scan.

4. Conclusions

CuS were prepared and characterized by Z-scan for nonlinear optical properties and calculated with different concentrations. The sample showed self-focused phenomena and a positive non-linear refractive index while the non-linear absorption index showed absorption Saturation.

This demonstrated that the prepared thin films can be utilized in nonlinear optical devices as a convex lens and also exhibit good optical properties, make it workable to convert solar energy. The sample showed self-focusing results and a positive non-linear refractive index while the non-linear absorption index showed saturation absorption and this showed that the sample can be used in non-linear optical devices as a convex lens as well as good optical properties, which makes it applicable to solar energy conversion.

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