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Effect of the thickness on the optical properties of nanostructure CuS thin films

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Abstract:

At this work, nanostructure copper sulfide (CuS) thin films at different temperature of substrate and thickness (120,200,750) nm have been acquired by chemical spray pyrolysis method. The X-Ray Diffraction (XRD) measurements of all films appeared polycrystalline structure and possessed a hexagonal phase with strong crystalline orientation (103) with crystal size equals approximately 80 nm by using atomic force microscopy (AFM). The linear optical measurements showed that nanostructure CuS thin films have direct energy gap. The energy gap was decreased with increasing thin films thickness. Nonlinear optical properties experiments were performed using Q-switched 1064 nm Nd:YAG laser Z-scan system. The nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) were estimated at different thicknesses of nanostructure CuS thin films for different intensities of laser. n_2 and β were decreased with increasing intensity of incident laser beam . Also they were reduced with increasing the nanostructure CuS thin films thicknesses. Also the type of β were two and three photon absorption , type of n_2 were positive nonlinear reflective index and n_2 were self-focusing nonlinear refractive index for all samples .

Introduction:

Copper sulfide is an important p-type semiconductor; also exhibits mixed electronic and ionic conduction and have recently attracted considerable attention as a candidate for the fabrication of nanoscale resistive switches due to the miniaturization and downsizing limits of the present day semiconductor devices[1].

Copper sulfide was used for the fabrication of crossbar switches, and the potential for the fabrication of reconfigurable large scale integrated circuits that employ such crossbar switches was demonstrated. Furthermore, a nonvolatile memory chip was also fabricated using such nanoscale switches[5].

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 [8].

The high intensity of laser beam can cause new types of physical effects, referred to as nonlinear optical processes. These effects with the optical constants of the material, either the absorption coefficient, the refractive index, or both. The term nonlinear derives from the expression for the polarization of the material P induced by the electric fields E associated with the optical beams[11].Finally due to their structural, electrical and optical properties, copper sulfides thin films are widely used as semiconductor and/or absorber materials with application in electronics, photovoltaic cells, and tubular solar collectors. Among these, CuS (covellite) thin films are known to exhibit metal like electrical conductivity and to posses near-ideal solar control characteristics[7].

The aim of present work is prepared nanostructure CuS thin film by chemical spray pyrolysis method and studies the structure and the linear and nonlinear optical properties of it. Also the our group researchers measured the electrical properties of nanostructure CuS thin film in another paper .

Experimental work:

Thin films of nanostructure (CuS) were prepared using copper acetate $Cu(CH_3COO)_2$, thiourea $SC(NH_2)_2$ with distilled water. The concentration of solution was 0.05 M .The nanostructure CuS films were formed at different temperature of the substrate (200,300,400) °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. Nanostructure CuS thin film was formed according to the following chemical reaction:

$$\mathbf{Cu(CH_3COO)_2+CS(NH_2)_2+2H_2O \rightarrow \underline{CuS}+2NH_4+CO_2+2CH_3COOH} \quad .....(1)$$

Different in temperature of the substrates lead to different in thickness of CuS . The film deposited in temperatures (200,300,400) C were in thickness (750, 200, 120) nm, respectively.

After CuS thin films were prepared, some measurement had be done involve structure measurement, linear optical properties measurement, nonlinear optical properties measurement.

The linear optical constants (refractive index - **n**- as well as the absorption coefficients - α , Extinction coefficient (K) and Real and Imaginary part of dielectric constant ε_1 and ε_2) can be found from transmittance spectrum of the films by the following equations:

$$\alpha = \frac{2.303 \times A}{t} \qquad \text{.......................... (2)[13]}$$

Where A is absorbance spectrum

t is thickness of thin films

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \qquad \text{................ (3)[15]}$$

Where R is reflectance and it equal R=1-T-A

$K = \alpha \lambda / 4\pi$ ………..………… (4)[14]

Where

λ is wavelength.

$$\varepsilon_1 = n^2 - k^2 \text{ ....…………………(5)[16]}$$

$$\varepsilon_2 = 2nk \text{ ... ...………………(6)[16]}$$

Results and Dissuasions:

X-Ray measurements :

The structure of the CuS thin films have been examined by XRD method using model (Shimad Zu 6000- Japan) . From figures (1-a), (1-b) and (1-c) XRD patterns of various CuS thin films deposited at different thickness for different temperature of substrate were shown. It is seen from the XRD patterns that the thin films showed a polycrystalline hexagonal structure the narrow peaks indicating 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 CuS (covellite) with lattice constant of a=3.792 A° and c=16.344 A°. This means that this plane is suitable for crystal growth.

Linear optical properties:

The nanostructure CuS thin films were tested using UV-VIS spectrophotometer type (SP3000, Optima, and Japan) for measuring the transmission (T). Figure (2) shows the optical transmittance spectra of nanostructure CuS thin films . Thin films are 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 lower thickness (120 nm), transmittance decreases slightly with the increasing of film thickness. This behavior is attributed to the increase the number of atoms with the thickness that leads to the increase of the number of collisions between incident atoms, which in turn, leads to the increase of absorption and decreasing transmittance.

Figure (3) shows the variation of (α) with photon energy $(h\nu)$ for (CuS) thin films. 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 see that absorption coefficient having values ($\alpha > 10^4 cm^{-1}$) which leads to increase the probability of occurrence direct transition. whereas the absorption coefficient is increasing with thickness decreasing. This can be linked with the formation stage and with increase in grain size and density of layers and it may be attributed to the light scattering effect for its high surface roughness.Also the extinction coefficient as a function of λ takes the same behavior of α as a function of hυ (eV) .

From figure (4) the behavior of refractive index with wavelength is the same of reflectance as a function of λ curve . Linear refractive index were increased directly with wavelength, afterward, they are slowly decreased. Also (n) are increased with increasing thicknesses .

The variation of ε_1 and ε_2 versus wavelength in the range (400-1100) nm at different thicknesses are shown in Figure (7) and (8). The variation of ε_1 and ε_2 with the increase of the wavelength of the incident radiation is due to the change of reflectance and absorbance. The behavior of ε_1 is similar to that of the refractive index because of the smaller value of k^2 compared with n^2, while ε_2 mainly depends on the k value, which are related to the variation of absorption coefficient. ε_2 represents the absorption of radiation by free carriers. It is observed that ε_1 increases with increasing thicknesses , and this attributed to the same reason mentioned previously for the refractive index, while ε_2 decreases with increasing of thicknesses and this is due to the similar interpretation discussed previously for the extinction coefficient.

Figure (7) show the direct energy gap. The energy gap decreased with increasing nanostructure CuS thin films thickness.

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

The coefficient B (taus slope) in the equation (7) has been obtained from square of the slope of straight line of Figure (8) and the values of Eg and B is tabulated in the table (1). From the table (1), we can observe that B is increased with the decreasing thickness. We Known 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.

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

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, which is shown in Figure (8) the reciprocal of the slope of the linear part from equation (8) give the value of E_u. The Urbach energy gives information about localized state in the band gap and its values tabulated in table (1) .From table (1) Urbach energy was reduced with the increasing of thickness .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.

Nonlinear Optical Properties:

The nonlinear optical properties were measured for nano CuS thin films at different thickness and different temperature of substrate. Different intensities (1.63, 2.44 and 3.26) GW/cm^2 were used Q-switched Nd:YAG laser 1064nm respectively.

Nonlinear Refractive Index:

The normalized transmittances of Z-scan measurements as a function of distance from the focus laser beam to the film. Figures (9) show these measurements for CuS thin films at different thickness and at 1064 nm for intensity1.63GW/cm^2.

The transmittance was increased directly with decreasing thickness. From all thickness of CuS and intensities can observe the positive nonlinear refractive index .From figure show all film behaviors were self-focus NLR.

. 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.

Nonlinear Absorption Coefficient:-

The nonlinear absorption coefficients β of CuS 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 CuS thin films at different thickness and intensities at 1064 nm are shown in (10).The behavior of transmittance started linearly at different distances from the far field of the sample position (-Z). 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=1064 nm, E=1.165 eV .Also the energy gap of thin films 119nm , 201 nm and 757 nm were 2.6 eV ,2.5 eV and 2.2 eV , respectively . Thus the condition 1E<Eg<2E for thickness of film 757 nm and 2E<Eg<3E for thickness of films 119 nm and 201 nm ,respectively .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 .

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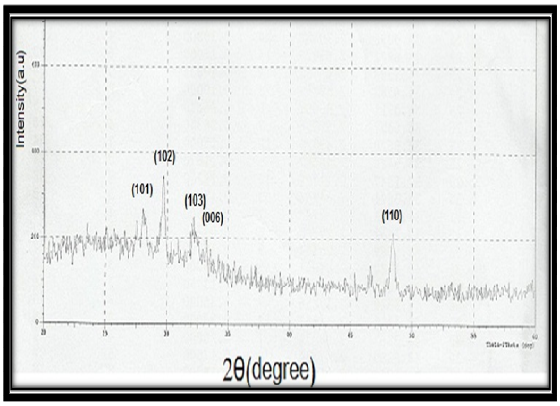

Figure (1-a): X-ray diffraction pattern of CuS thin film having 120 nm thickness.

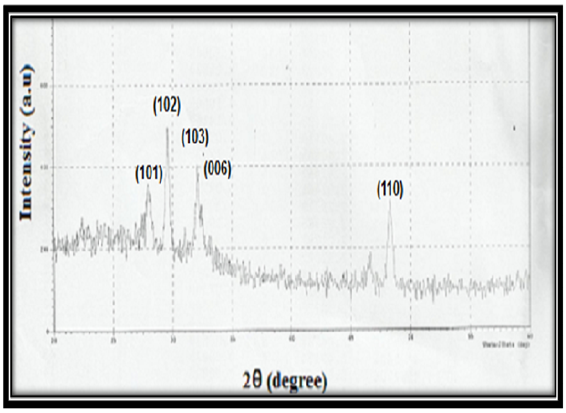

Figure (1-b): X-ray diffraction pattern of CuS thin film having 200nm thickness.

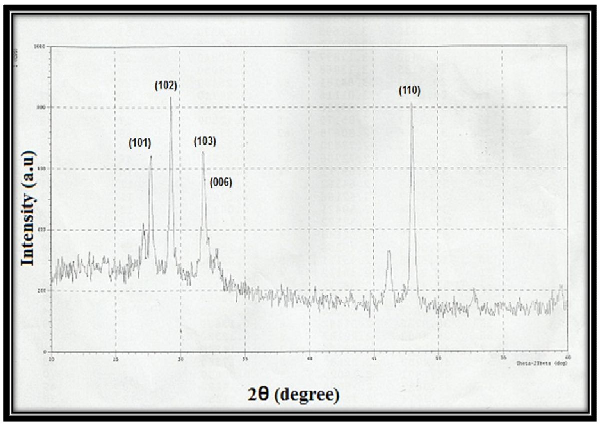

Figure (1-c): X-ray diffraction pattern of CuS thin film having 750 nm thickness.

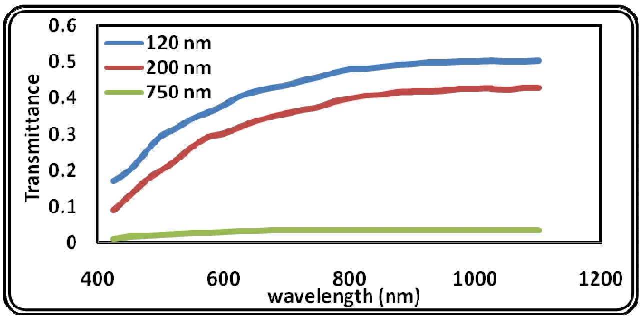

Figure (2): Transmittance spectra of nanostructure CuS thin films at different thicknesses .

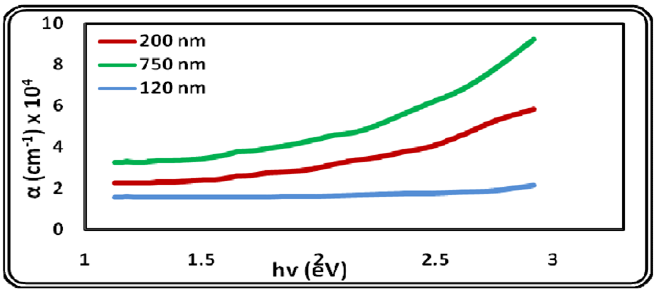

Figure (3): Absorption coefficient as function of energy photon for different thickness of nanostructure CuS thin films.

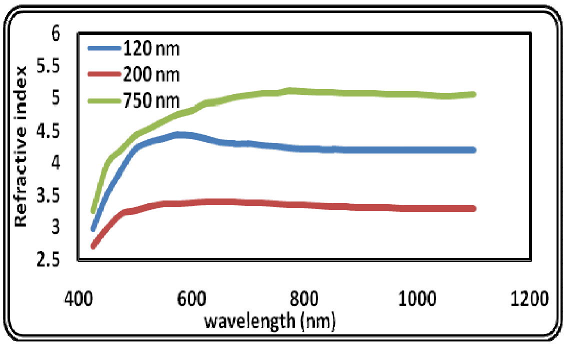

Figure (4): Refractive index as function of wavelength for different thickness of nanostructure CuS thin films.

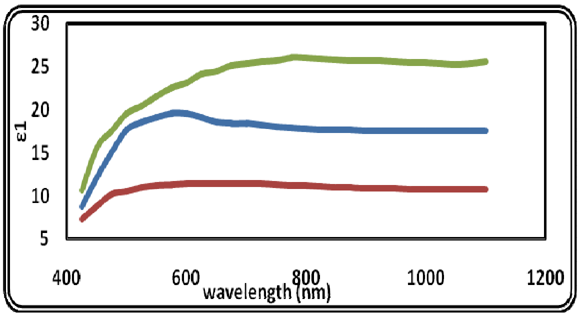

Figure (5): Real dielectric constant (ε_1) of nanostructure CuS thin films.

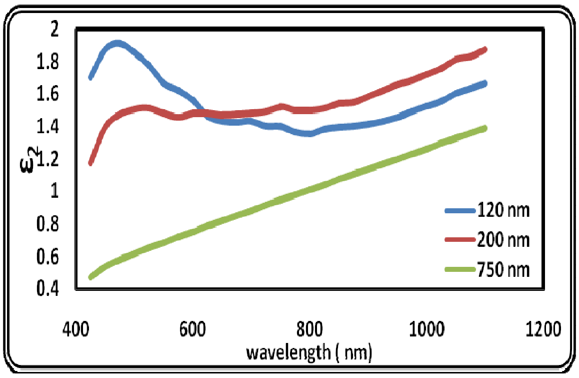

Figure (6): Imaginary dielectric constant (ε_2) of nanostructure CuS thin films.

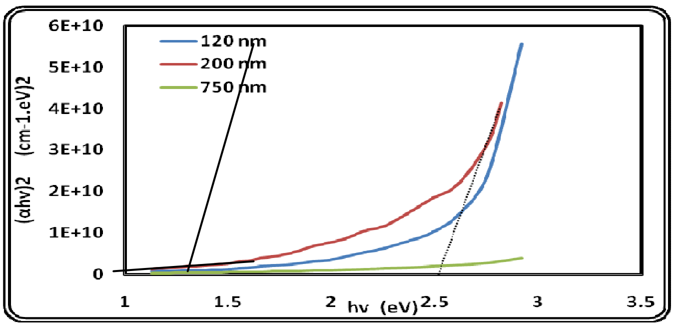

Figure (7): $(\alpha h\nu)^2$ as function of energy photon for different thickness of nanostructure CuS thin films**.**

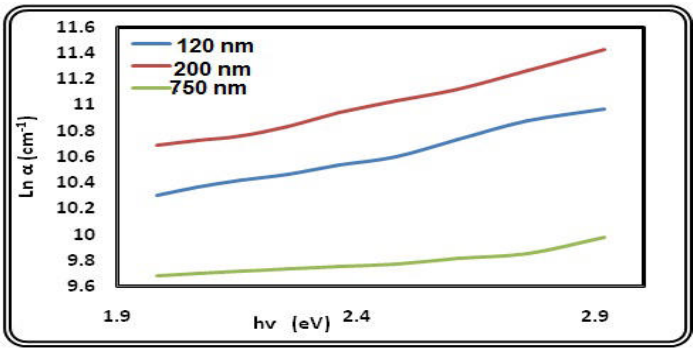

Figure (8): The variation of Ln α with photon energy for nanostructure CuS thin films.

Table (1): Eg , B and Eu.

thickness (nm)	E_g eV	$Bx10^4$ $eV^{1/2}$. cm^{-1}	E_u eV^{-1}. Cm^{-1}
120	2.6	10	1.3
200	2.5	5	1.4
750	2.2	3	2.6

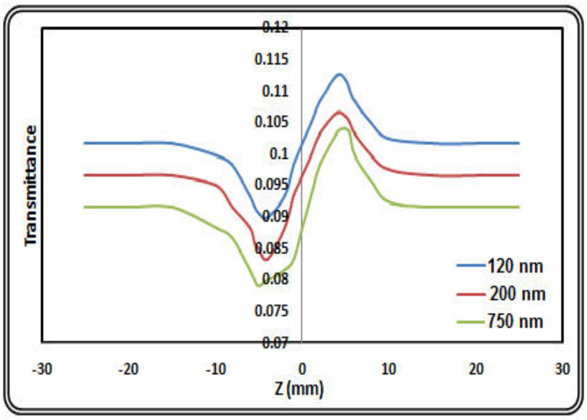

Figure (9) : Closed-aperture of nanostructure CuS thin films at different thickness for 1.63 GW/cm^2 at 1064 nm

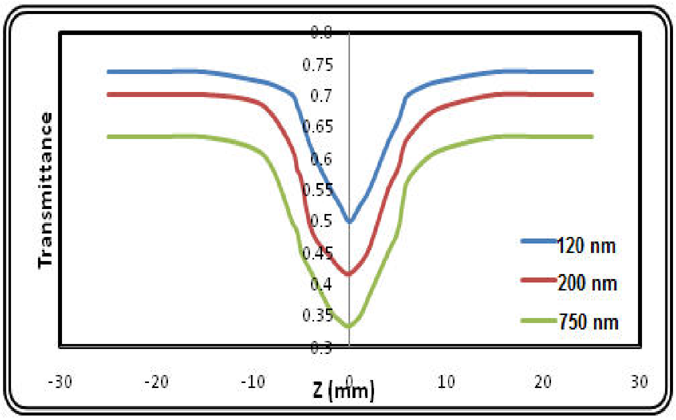

Figure (10): Open-aperture of nanostructure CuS thin films at different thickness for 1.63 GW/cm^2 at 1064 nm.