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Review Article

INVESTIGATION OPTICAL PROPERTIES OF CUZNSNS THIN FILMS PREPARED BY PULSE LASER DEPOSITION

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Abstract
The prepared samples of thin-film by laser ablation method were achieved. Powders of (CZTS) copper (Cu), zinc (Zn), tin (Sn) and Sulfur (S) of and then compressing by approximately 3 tons in Pellets form. The samples were ablated by using Neodymium-YAG laser with different laser energies (400mJ, 500mJ, 600mJ, 700mJ, 800mJ) and number of pulses (300)pulse, frequency (6Hz)and wavelength(1064) nm obtained the plasma plume at 10^{-5}mbar pressure. Results indicate the optical properties of the films, which were prepared ,have been determined by using the optical transmittance measurements in the spectral region from 400 to 1000 nm. Transmittance results were upper than 90% which make these films suitable for sensor applications.. The optical energy gap of Cu_2ZnSnS_4 compound thin films was a direct allowed transition and decrease of values (2.8-1.8eV), if the laser energy is increased, also the increasing of thickness from (130.26 - 176.83 ±7) nm of the film as a result to the increase laser energy. The optical constants such as refractive index, extinction coefficient and dielectric constant have been calculated for the prepared films.

Keywords
thin film, nanoparticle, CZTS, optical, Transmittance, optical energy gap, refractive index , pulse laser deposition.

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INTRODUCTION

is a quaternary semiconducting compound Includes I2-II-IV-VI4 aggregates such as copper (Cu), zinc (Zn), tin (Sn) and Sulfur (S), The CZTS can be obtained by replacing the trivalent In / Ga element with divalent Zn and tetravalent Sn which form the kesterite phase [1]. CZTS is a glycoprotein compound used as a sorbent in solar cells [2]. It was discovered more than twenty years ago by researchers Ito Nakazawa [3] they were able to prepare this compound as a thin film using spray technology. this compound has a direct energy gap of about 1.4 - 1.5eV and has an absorption coefficient in the visible area greater than ($10^4 cm^{-1}$) and a positive conductivity [4], it's very low cost compared to light absorbing compounds such as Cu (InGa) (S, Se), CuInS2[5]. high thermal stability as well as the use does not affect the environment due to the lack of noble elements and very toxic substances, The composition of Cu2ZnSnS4 consists of a quadrilateral type This compound has been prepared in several different ways [6].

PRACTICAL PART

To prepare the thin films of Cu_2ZnSnS_4 of different laser energies (400mJ, 500mJ, 600mJ, 700mJ, 800mJ) by using laser ablation system which consists of two parts, the first part of discharge chamber that contains the target holder and holder for substrate and a window for the passage of the laser light made light of the pack quartz, as well as thermal and double valves dump ,where it is the subject of substrate vertically on the target holder, where the distance between them is 4cm and the pressure inside the room deposition 10^{-5} mill bars, which can be accessed using the discharge rotary and diffusion vacuum respectively.

The second part consists of a system of Nd-YAG laser which operates at wavelength 1064nm, and using energies (400mJ, 500mJ, 600mJ, 700mJ, 800mJ) for five samples and 6 HZ frequency and number of pulses used was 300 pulses constant.

The laser beam is focused on the target using the focal lens dimension to distant subjects 30cm inclination angle almost 45^0 surface.

The powders of pure CZTS materials are, then compressed these powders using hydraulic piston, Under pressure 3Ton, getting tablets thickness 3 mm, diameter of 2 cm. It was placed inside the deposition chamber on the target holder, ablated these discs using a laser Nd-YAG focused of the laser beam on the target using the lens focal dimension 30cm surface.

The optical properties of the thin films prepared were measured by UV-visible spectrometers ,Absorptance ,Transmittance,α , Eg ,n, k_o, ε_r, ε_i

RESULTS AND DISCUSSION

Figure (1) shows the relationship between absorbance and wavelength of CZTS films prepared with different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse. Through the figure, we notice that the absorbance decreases with wavelength for all the prepared thin films when increasing laser energy .This physically means that incident photon is not able to excite the electron and transfer it from valence band to the conduction band because the energy of incident photon is less than the value of the energy gap value of the semiconductor .This leads to the absorbance decrease with increasing of wavelength. It is also noticeable that the absorbance decreases with increasing laser energy. This confirms CZTS atoms entry within the crystal structure of the prepared film, and configure localized levels within the energy gap that led to the absorption of photons with a law energies. The shifts of absorbance spectrum to shorter wavelengths (higher energies) with the increase of laser energy for all thin films may be attributed to the crystallization of film structure by increasing the grain size, Absorption spectra optical depends on the chemical composition, crystal structure, energy of the incident photon, film thickness, and film surface morphology.

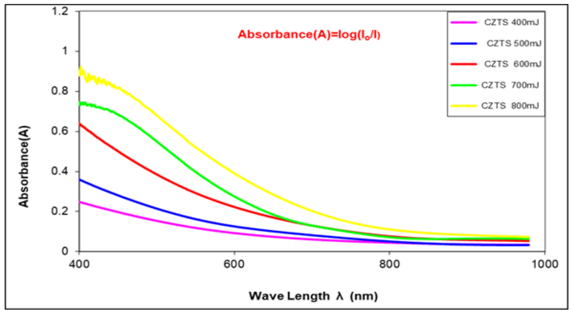

Figure (1): Absorbance spectrum as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

Figure (2) shows the relationship between transmittance and wavelength of CZTS films prepared with different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse. Transmittance demonstrated behaviour opposite of absorbance as shown transmittance of prepared films increases with increasing of laser energy that could due to the increasing crystallinity of CZTS due to formation of a new localized levels under the conduction.

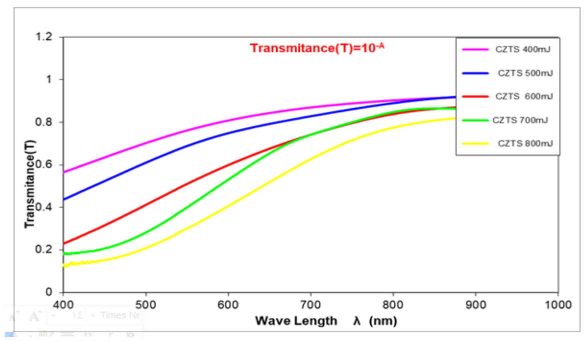

Figure (2): transmittance spectrum as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse

Figure (3) shows the optical absorption coefficient as a function of incident wave length of CZTS films prepared with different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse .It has been noticed that all the thin films prepared have high absorption coefficient (α >104cm-1) which indicates the increase of the probability of the occurrence of direct transitions. The Figure shows that the absorption coefficient of the films decreases gradually with wave length when the laser energy is increased. This is because the absorption value coefficient indicates the ability of the film material to absorb the energy of the falling radiation as well the increase in laser energy increases the thickness of the prepared films.

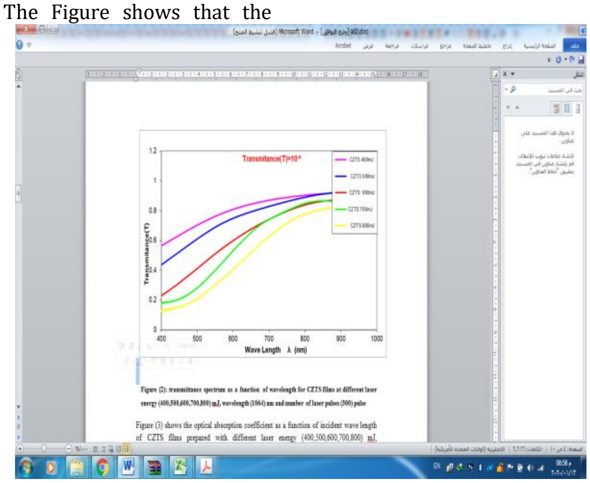

Figure (3): Absorption coefficients as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse

From Figure (4), the optical energy gap of Cu_2ZnSnS_4 films deposited on glass substrates was calculated under pressure (10-5mbar), number of pulses (300pulse) and frequency (6Hz) and different laser energies (400mJ, 500mJ.600, mJ, 700mJ, 800mJ), The figure shows the relationship between $(\alpha h\upsilon)^2$ on the y-axis and photon energy (hυ) on the x-axis, Where the optical energy gap of the allowable direct transition from the tangent extension of the curve was calculated to meet the photon energy axis at point $(\alpha h\upsilon)^2 = 0$, since intersection point represent the optical energy gap of the allowed direct electronic transitions and was found to decrease as laser energy increased this is due to the increase in the number of spot levels between the conduction band and valence band and due to the conversion of CZTS compound from (p) to (n) after increasing the laser energy from 400mJ to 800mJ, This means that the optical energy gap values can be controlled by changing the laser energy when prepared CZTS films. We observed that when calculating the energy gap, we found that its value ranges between (2.8 – 1.8eV). We noticed an increase in laser pulse energy that the energy gap is decreasing ,As a result of the irritation of secondary levels within the energy gap and as a result, the width of the energy gap decreases and deposited the largest number of grins on the surface of the substrate .Table (1) shows the optical energy gap values for CZTS films at different laser energies, the energy gap decreases by increasing the laser energy when preparing the films of the compound.

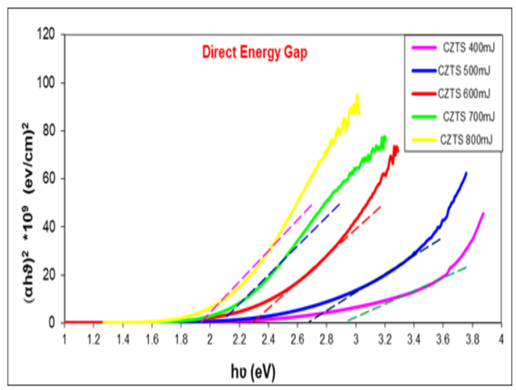

Figure (4): The optical energy gap for the allowable direct transition for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

Table (1): The values of optical energy gap for CZTS thin films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

Sample	E_g (eV)
$CZTS_{400mJ}$	**2.8**
$CZTS_{500mJ}$	**2.5**
$CZTS_{600mJ}$	**2.3**
$CZTS_{700mJ}$	**2.1**
$CZTS_{800mJ}$	**1.8**

The relationship between extinction coefficient and wavelength of deposited CZTS films is shown in figure (5). In general, it is clear that The extinction coefficient (k) decreases with the increasing laser energy for all prepared samples. It is clear that k value for CZTS films, In general the behavior of k similar to the behavior of α. This is attributed to the same reason mentioned previously, since the increasing laser energy of CZTS samples decreases the optical energy gap as a result of absorbance decrement.

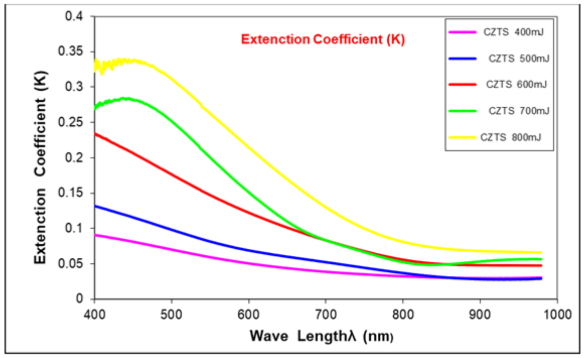

Figure (5): Extinction coefficient as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

The variation of the refractive index versus wavelength in the range of (396–996) nm for CZTS films at different energy of laser are shown in figure (6). It can be noticed from this figure the refractive index (n) increases when the laser energies increase in the area of short wavelengths (area of high energies) and then decrease with the increase of laser energies in the area of long wavelengths. This behaviour can be explained on the basic of that increases energy of laser leads to make prepared samples more dense and the change in crystalline structure, which in turn increases propagation velocity of light through the sample which results decreasing of the refractive index (n) values at long wave lengths.

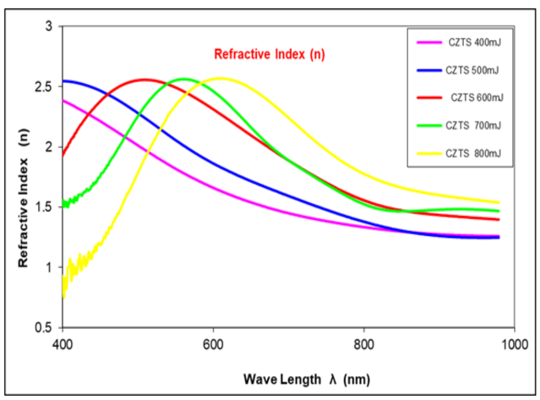

Figure (6): Variation of refractive index as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

Figure (7) shows the real dielectric constant of CZTS films prepared at different laser energies (400,500,600,700,800) mJ, wavelength (1064) nm and the number of laser pulses (300) pulse as a function of wavelength, Noting from the figure that the real dielectric constant increases when the laser energies increase in the area of short wavelengths (area of high energies) and then decrease with the increase of laser energies in the area of long wavelengths. Figure (8) illustrates the change of the imaginary dielectric constant of CZTS films in different laser energies (400,500,600,700,800) mJ, wavelength (1064) nm and the number of laser pulses (300) pulse as a function of wavelength. It is noted from the figure that the value of the imaginary dielectric constant increases when the energies of the laser in the area of short wavelengths (high energies) increase and then decrease with the energies of the laser in the area of long wavelengths.

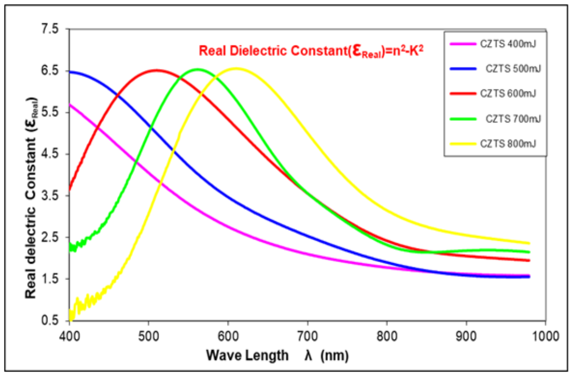

Figure (7): Real dielectric constant as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

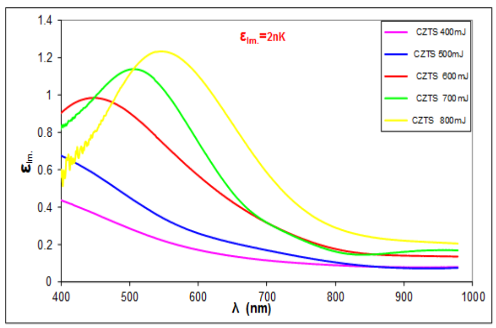

Figure (8): Imaginary dielectric constant as a function of wavelength for CZTS films at different laser energy (400,500,600,700,800) mJ, wavelength (1064) nm and number of laser pulses (300) pulse.

CONCLUSIONS

1- The optical study revealed that the films were highly absorbed with a direct allowed type of transition.

2- Decrease in the energy gap by increasing the energy of the laser pulse due to the larger grain size, which leads to an increase in thickness and decrease in the energy gap.

3- The optical absorption coefficient of all films prepared by pulsed laser deposition technique at different laser energies and stability of the rest of the laser parameters is greater than $10^4 cm^{-1}$ indicating direct electronic transitions between the CZTS film conduction and valence bands.

4- Most optical constants have the highest values at the short-wave (ultraviolet) region, which is rapidly reduced by increasing the wavelengths of the electromagnetic spectrum when laser energies are increased.

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