Fabrication a device Hetrojunction of Compound Cu_2ZnSnS_4 Films and study the Electrical Properties of it by Pulse Laser Deposition

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Abstract:
The prepared samples of compound thin-film by pulse laser deposition 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 by continuous conductivity and using Hall phenomena systems and I-V characteristics in light and dark states .The electrical results show that continuous conductivity indicated that conductivity increases with increasing temperature, and decreases conductivity with increasing film thickness when increasing laser energy, It was found that the electrical conductivity has two values for the activation energy Ea1 and Ea2 this is due to two types of transfers ,The first activation energy is the transition between positional levels within the energy gap that occurs by the jump method and the second activation energy represents the transition between farther levels within the energy gap by the method of thermal stimulation. carrier type changes of the films of the CZTS compound from p- type to n-type when the laser energy increases, so the density of carriers, conductivity and resistivity is disparate, while the mobility decreases with increasing laser energy. The I-V characteristics in light and dark states Show that there is decrease with the disparit of current values in the dark state and an increase in the sensitivity of the samples after lighting in the forward and reverse bias ,and the best efficiency efficiency of heterojunction is with a value of (4.1402813) when depositing the type (n) film of the CZTS sample on the Si (p) substrate at laser energy (800mJ). As for the efficiency of the heterojunction prepared, it is noted that it increases at the energy of the laser (800mJ) Si (p) /CZTS800mJ (n) then it starts to decrease when the (n) film is deposited on the (n) substrate, Because the electron density increases when the laser energy increases. 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.

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I. 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 (104cm-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].

II. Practical Part

To prepare the thin films of Cu2ZnSnS4 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. It was placed inside the deposition chamber on the target holder, and ablated these discs using a laser Nd-YAG focused the beam on the target passing through the lens. A Hall effect(HMS-3000) are carrying out on the samples by depositing gold electrodes by ionic coater using a mask and affected magnetic field with intensity (0.55Tesla) and power supply (0-2 V) with digital millimeters are used. Also I–V characteristics of hetrojunctions Si(p)/ CZTC and Si(n)/ CZTS were measured in light and dark states. The optical energy gap also were found at different laser energies of compound Cu_2ZnSnS_4 thin films by using spectrometer system.

III. Results and Discussion

The electrical conductivity as a function of temperature of CZTS films at different laser energies (400,500,600,700,800) mJ thin films deposition on glass is shown in Figure (1). It is seen that conductivity increased with temperature. This seems to be a normal behavior as one of semiconductor properties, due to the increasing carrier concentration with temperature. We also note that the conductivity decreases at high laser energies (700,800)mJ. It is very useful to determine in the extrinsic range the activation energies of impurity centers and in the intrinsic range the main energy gap. By using equation

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{k_B \check{T}}\right) \quad \cdots\cdots\cdots\cdots (1)$$

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Where:

E_a: is the activation energy.

Ť: is the absolute temperature.

σ_o: is the minimum electrical conductivity at 0K.

plots the (Lnσ) vs. reciprocal of the absolute temperature (10^3/T), we can measure the activation energy by taking the slope of straight lines of ($-\Delta E/k_B$). From Figure (2) it is found that there are two phases of conductivity all through the warming temperature range. The first activation energy (E_{a1}) occurs at lower temperature and this activation energy is due to conduction of the carrier excited into the extended states beyond the mobility edge, while the second activation energy (E_{a2}) occurs at higher temperature and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands. These two conduction mechanism means that there are two transport mechanisms. It was found that the electrical conductivity has two values for the activation energy E_{a1} and E_{a2} this is due to two types of transfers ,The first activation energy is the transition between positional levels within the energy gap that occurs by the jump method and the second activation energy represents the transition between farther levels within the energy gap by the method of thermal stimulation[7].Table (1) shows that the value of Ea_1 is smaller than values of Ea_2 .This indicates that the conductivity depends on the temperature where conductivity proportional with $T^{3/2}$ [8].

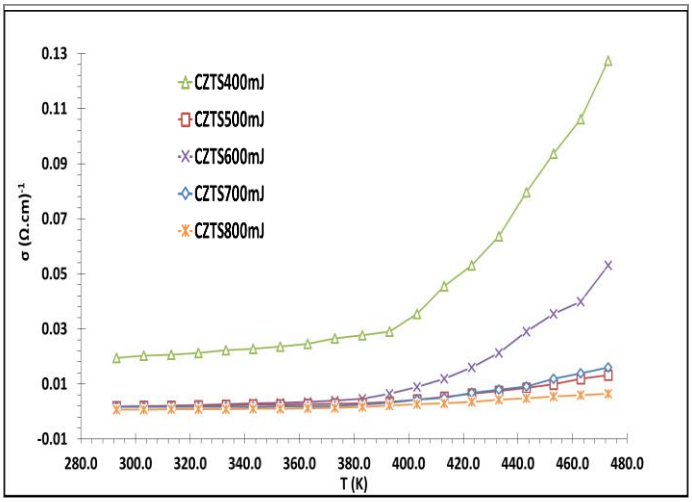
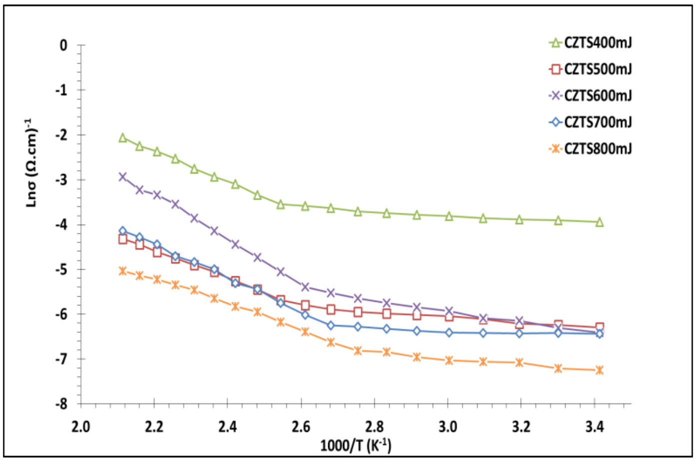


Figure (1): Variation of $\sigma_{D.C}$ versus temperature for CZTS thin films at different laser energies.



Figure(2): Lnσ versus 1000/T for CZTS thin films at different laser energies.

Table (1): D.C. conductivity parameters for CZTS thin films at different laser energies.

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Sample name	Ea1 (eV)	Range (K)	Ea2 (eV)	Range (K)	σRT (Ω.cm) $^{-1}$*10^3
$CZTS_{400mJ}$	0.037	283-363	0.279	363-473	19.419
$CZTS_{500mJ}$	0.048	283-363	0.236	363-473	1.844
$CZTS_{600mJ}$	0.152	283-363	0.399	363-473	1.642
$CZTS_{700mJ}$	0.018	283-363	0.308	363-473	1.608
$CZTS_{800mJ}$	0.017	283-363	0.244	363-473	0.709

Hall coefficient (RH) is important to know the electrical properties, (RH) depend on the value of incident magnetic field on the film is located vertically in front that field. Studied Hall effect measurements of Cu2ZnSnS4 films have been at different laser energies (400,500,600,700,800mJ) for the purpose of identifying the type of charge carriers, their concentration, Hall coefficient values, resistivity, and conductivity and mobility at room temperature, Where it was found that the carrier type of the CZTS films is a positive type (p-type) of the positive hall effect (RH) value, As the laser energy increased, the CZTS films were converted from p-type to n-type from the negative hall effect (RH) value, The reason for this transformation is the increase in laser energy, which has resulted in a decrease in the grain size of the film in addition to that the values of the Hall coefficient are disparit for the n- type due to the increase in laser energy due to the change in the granular size and the granular assemblies on the film due to deposition.It is noted from Table (2) by using a computer program that the conductivity(σ), resistivity(ρ),concentration (nH) and hall coefficient(RH) values are disparit for the type of carriers (n) But the mobility values decrease as the laser energy increases.

Table (2): Hall parameters for CZTS films at different laser energies.

Sample Name	**Concentration of Carriers n_H Cm^{-3}**	**Conductivity σ(Ω.Cm)$^{-1}$**	**Resistivity ρ(Ω.Cm)**	**Mobility μ_H(Cm^2/V.s)× 10^2**	**Hall Effect RH(Cm^{-3})**	**Type of Carriers**
$CZTS_{400mJ}$	**5.632×10^{11}**	**1.120×10^{-6}**	**8.931×10^{5}**	**1.243**	**1.110×10^{7}**	**p-type**
$CZTS_{500mJ}$	**-7.968×10^{10}**	**1.200×10^{-6}**	**8.337×10^{5}**	**9.398**	**-7.835×10^{7}**	**n-type**
$CZTS_{600mJ}$	**-2.042×10^{11}**	**1.510×10^{-6}**	**6.620×10^{5}**	**4.618**	**-3.057×10^{7}**	**n-type**

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$CZTS_{700mJ}$	**-3.191×10^{10}**	**1.360×10^{-6}**	**7.353×10^{5}**	**2.661**	**-1.956×10^{8}**	**n-type**
$CZTS_{800mJ}$	**-9.130×10^{10}**	**2.065×10^{-6}**	**4.844×10^{5}**	**1.412**	**-6.837×10^{7}**	**n-type**

The study of current-voltage properties in state dark and lighting is important because it is a clear indication of the possibility of using the CZTS compound as a light-sensitive material (solar cell). Where we observe the effect of light is evident in the change of current and voltage values for the samples prepared for the CZTS compound at different laser energies (400,500,600,700,800mJ). Where Figure (3) shows that values the current in the dark state are less than the lighting state in the forward and reverse biases of the Si (p) type film at 400mJ and turns CZTS semiconductor from p-type to n-type when the laser energy is increased ,Where we note that the current values are disparit for the forward and reverse bias when changing the laser energy values (500,600mJ) as in figures (4), (5). Then we notice an increase in the sensitivity of the samples after lighting and the resistance is higher at energy (700mJ) as in Figure (8) (6) in both forward and reverse biases and effect of the samples is higher in the dark state, This is due to the change in the grain sizes and aggregations grain on Si (n) substrates. It is noted from Figure (7) that the electrical current of the Si (p) sample does not flow at laser energy (800mJ) in the dark state because of the high potential barrier formed at the junction (p-n) of the sampls the higher the laser energy however, the increase is evident when the (n) membrane is deposited on the Si (n) substrate due to a decrease in the potential barrier between (n-n) the difference in the concentration of carriers as in Figure (9) In lighting state and dark when the laser energy is (500mJ) and values of the current passing between (n-n) decrease at 600mJ, especially in dark state because of the decrease in the grain size, as in Figure (10), and the current resistance is higher due to the large potential barrier at (700mJ), as in Figure (11) for type (n-n) the difference in the concentration of carriers ,The current does not pass through the heterojunction in the dark state when the laser energy is increased to (800mJ) as shown in Figure (12) because the n- type carriers are not generated while the current resistance in the lighting state is higher in the forward bias than the reverse bias because changed the carriers concentration of n- type of the Si (n) substrate and deposited n- type has on the substrate of the CZTS sample. That increased sensitivity of the samples after lighting changes when the silicon sample is a type (p) over the type (n), as they differ in the density of carriers and its type because the heterojunction is anisotype, Si (n) / CZTS (p), Si (p) / CZTS (n). As for other sampels, for example Si (n) / CZTS (n), Si (p) / CZTS (p) at different laser energies (400,500,600,700,800mJ) it is observed that the density of the silicon carriers, whether it is the type (p-p) or the similar type (n-n) have the same values of density but the second side of the heterojunction may have the same density as the carriers of silicon type (p) and silicon type (n) but they are different in density for carriers of the compound, which relatively generates a different potential barrier, Due to the difference in density values then we note that the current values are disparit ,Which reduces its sensitivity to darkness. It is also noted from the previous figures that the current values are higher for the same voltage values in the lighting state due to the excitation of the heterojunction (p-n) when photons incident, which generate more carriers because of the breaking of the bonds that occur as a result of the incident, which increases the current values. As for the efficiency of the heterojunction prepared, it is noted that it increases at the energy of the laser (800mJ) Si (p) /$CZTS_{800mJ}$ (n) then it starts to decrease when the (n) film is deposited on the (n)

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substrate. Because the electron density increases when the laser energy increases and table (3) indicates open circuit voltage (V_{oc}) and short circuit current (I_{sc}), maximum voltages, current, fill factor, and efficiency of samplels from heterojunctions of the Si/CZTS compound. Using a computer program, it was found that these values are disparit and do not indicate an increase or decrease pattern, while it was noticed that the highest value of open circuit voltage is (50mV) for the Si (p) sample with a (n) type film deposited for the CZTS sample at a energy of (500mJ). It was noted that the best efficiency is with a value of (4.1402813) when depositing the type (n) film of the CZTS sample on the Si (p) substrate at laser energy (800mJ).

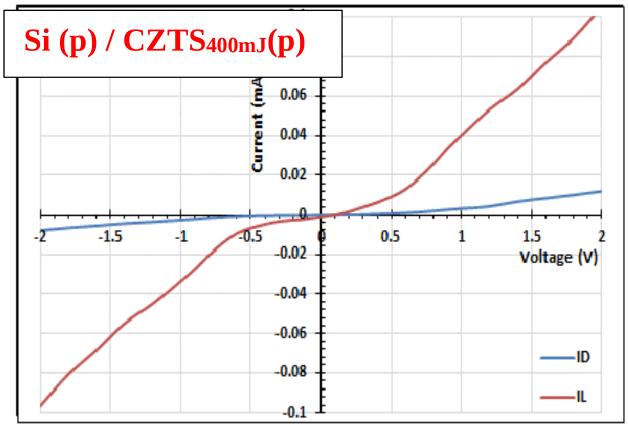

Figure (3) I-V Characteristics in Dark and Light for film Si (p) / $CZTS_{400mJ}$(p)

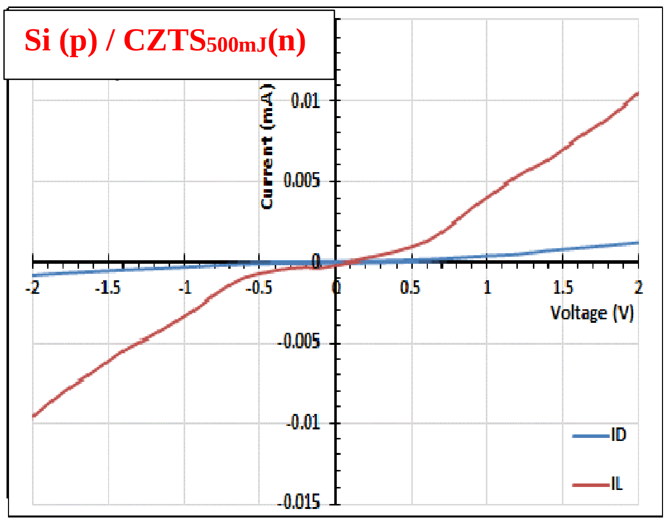

Figure (4) I-V Characteristics in Dark and Light for film Si (p) / $CZTS_{500mJ}$(n)

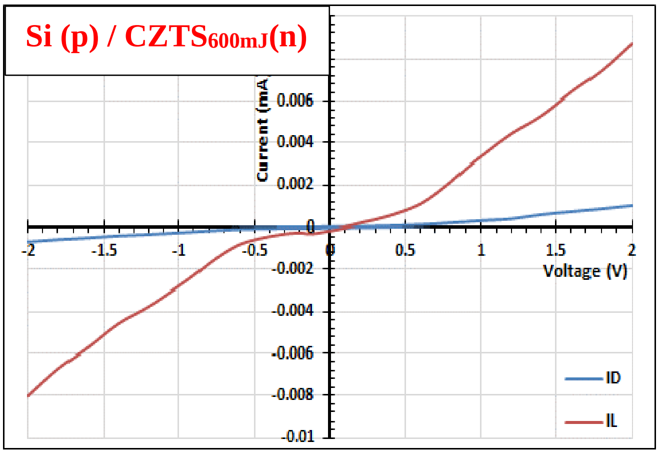

Figure (5) I-V Characteristics in Dark and Light for film Si (p) / $CZTS_{600mJ}$(n)

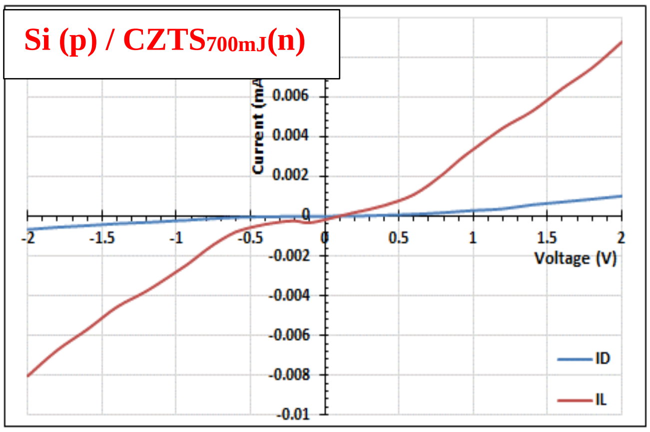

Figure (6) I-V Characteristics in Dark and Light for film Si (p) / $CZTS_{700mJ}$(n)

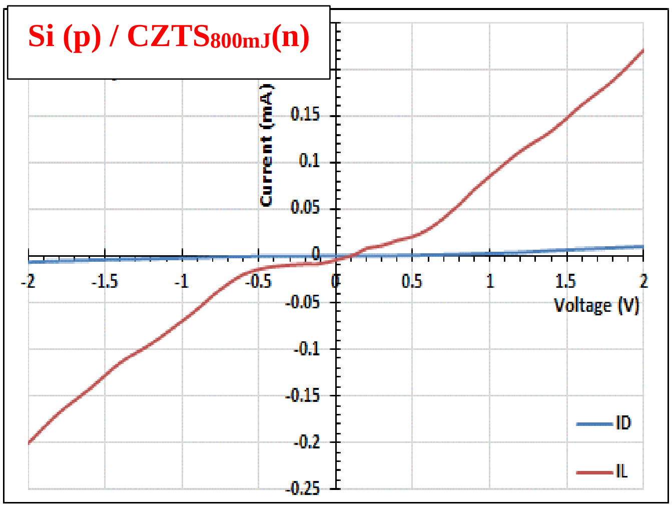

Figure (7) I-V Characteristics in Dark and Light for film Si (p) / $CZTS_{800mJ}$(n)

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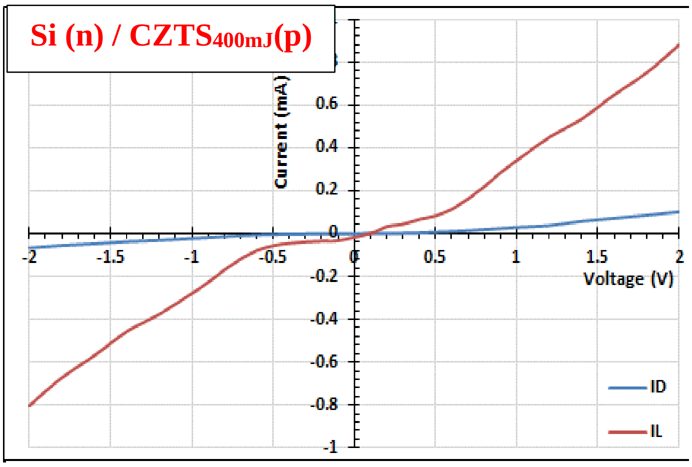

Figure (8) I-V Characteristics in Dark and Light for film Si (n) / $CZTS_{400mJ}$(p)

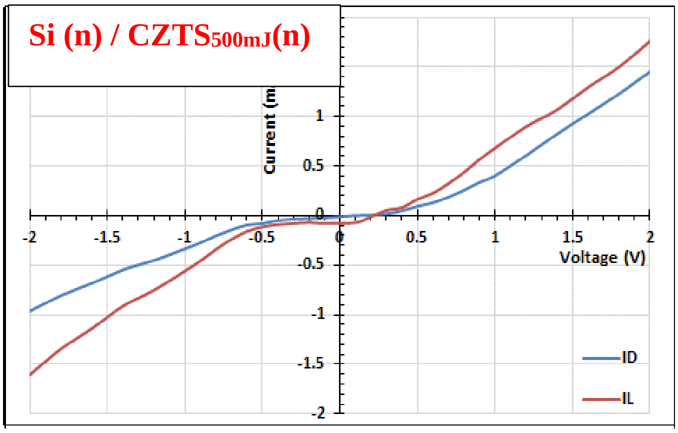

Figure (9) I-V Characteristics in Dark and Light for film Si (n) / $CZTS_{500mJ}$(n)

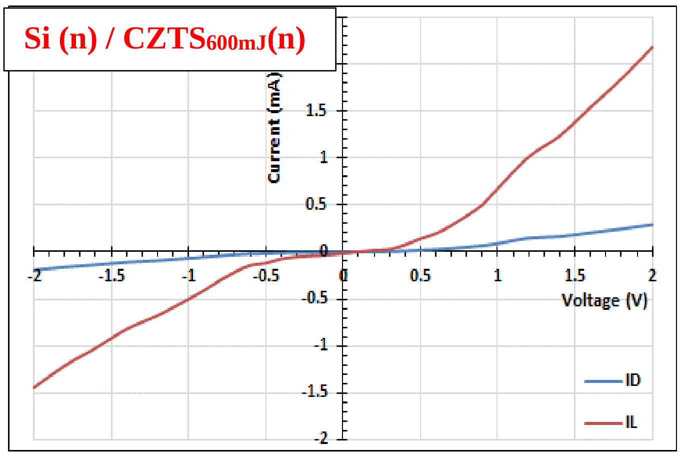

Figure (10) I-V Characteristics in Dark and Light for film Si (n) / $CZTS_{600mJ}$(n)

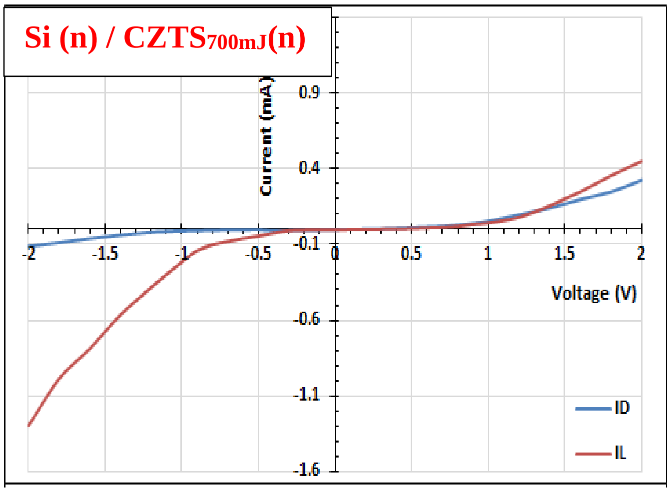

Figure (11) I-V Characteristics in Dark and Light for film Si (n) / $CZTS_{700mJ}$(n)

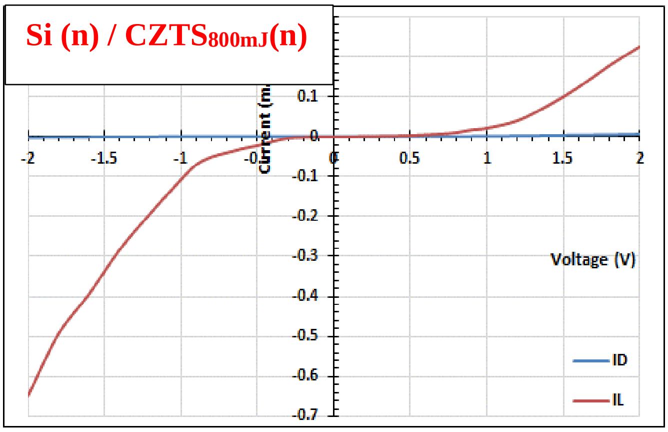

Figure (12) I-V Characteristics in Dark and Light for film Si (n) / $CZTS_{800mJ}$(n)

Table (3): Values Open Circuit Voltage, Closed Circuit Current and values Maximum for Voltage and Current, Fill Factor, and Efficiency for samples of heterojunction of Si(p,n) / CZTS at difrent laser energies.

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Sample	V_{oc} (mV)	I_{sc} (mA)	V_{max} (mV)	I_{max} (mA)	F.F	η%
Si (p)/$CZTS_{400mJ}$(p)	95.0000	0.0011	50	0.00052	0.25	0.0442177
Si (p)/$CZTS_{500mJ}$(n)	98.0000	0.00017	50.00	0.000059	0.18	0.0050170
Si (p)/$CZTS_{600mJ}$(n)	100.0000	0.00014	40	0.000058	0.17	0.0039456
Si (p)/$CZTS_{700mJ}$(n)	100.0000	0.00016	45	0.0001	0.32	0.0087464
Si (p)/$CZTS_{800mJ}$(n)	98.0000	0.0042	45	0.002103	0.91	4.1402813
Si (n)/$CZTS_{400mJ}$(p)	215.0000	0.07516	14	0.05515	0.05	1.3130952
Si (n)/$CZTS_{500mJ}$(n)	215.0000	0.07616	14.2	0. 56615	0.48	1.4230952
Si (n)/$CZTS_{600mJ}$(n)	80.0000	0.0154	40	0.007	0.23	0.4761905
Si (n)/$CZTS_{700mJ}$(n)	150	0.00175	100	0.001254	0.47662	0.213265306
Si (n)/$CZTS_{800mJ}$(n)	98	0.0009	90	0.00073	0.7449	0.111734694

IV. CONCLUSION

1- The results of continuous conductivity indicated that conductivity increases with increasing temperature, and decreases conductivity with increasing film thickness when increasing laser energy.

2- It was found that the electrical conductivity has two values for the activation energy Ea1 and Ea2 this is due to two types of transfers ,The first activation energy is the transition between positional levels within the energy gap that occurs by the jump method and the second activation energy represents the transition between farther levels within the energy gap by the method of thermal stimulation.

3- The carrier type changes of the films of the CZTS compound from p- type to n-type when the laser energy increases, so the density of carriers, conductivity and resistivity is disparit, while the mobility decreases with increasing laser energy .

4- We note a decrease with the disparit of current values in the dark state and an increase in the sensitivity of the samples after lighting in the forward and reverse bias.

5- It was noted that the best efficiency of heterojunction is with a value of (4.1402813) when depositing the type (n) film of the CZTS sample on the Si (p) substrate at laser energy (800mJ).

6- As for the efficiency of the heterojunction prepared, it is noted that it increases at the energy of the laser (800mJ) Si (p) /CZTS800mJ (n) then it starts to decrease when the (n) film is deposited on the (n) substrate, Because the electron density increases when the laser energy increases.

7- noticed that the highest value of open circuit voltage is (50mV) for the Si (p) sample with a (n) type film deposited for the CZTS sample at a energy of (500mJ), There is a variation in the values(I_{sc},V_{oc}, I_{max},V_{max},FF) when depositing isotype (p / p), (n / n) and anisotype (n / p), (p / n).

8- The optical energy gap of allowed direct transition decrease as increasing in laser energy and increased films thickness.

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