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Study some Electrical Properties of Cu_2ZnSnS_4 Thin Films Prepared by Pulse Laser Deposition

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دراسة بعض الخصائص الكهربائية لأغشية Cu_2ZnSnS_4 الرقيقة المحضرة بالترسيب بالليزر النبضي

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ABSTRACT

Background

Pulses increased the thin-film sample preparation was carried out via a laser ablation method. 5 tons of pressure which were used to compress powdered (CZTS) pellet form. Utilizing a Neodymium-YAG laser with a range of 700mJ laser energy, and the plasma plume was created at a pressure of 10^{-5}mbar utilizing at a frequency of 6Hz. Electrical Properties including Hall effect and electrical conductivity were investigated. According to Hall measurements, the films prepared were p-type at 200 pulses and changed to n-type as the number of pulses increased. They also had two activation energies (Ea_1 ,Ea_2). The conductivity was shown to increase as the number of pulses increased.

Materials and Method

A Neodymium-YAG laser with a range of 700mJ laser energy, and the plasma plume of 10^{-5}mbar were utilizing number of pulses at a frequency of 6Hz. The Hall effect and electrical conductivity were investigated.

Results

Hall effect and D.C were studied. According to the findings, the prepared films were p-type at 200 pulses and changed to n-type as the number of pulses increase. They also had two activation energies (Ea_1 and Ea_2).The electrical conductivity was shown to increase as the number of pulses.

Conclusions

Two activation energies (Ea_1 , Ea_2). Hopping method for moving the carriers between levels inside the energy gap and the thermal stimulation method for moving between other levels. The carrier type of CZTS compound films change from p-type to n-type as the number laser pulses increase.

Keyword: laser, pulses, conductivity, Hall effect, activation energies.

مجلة جـامعة بـابل للعلـوم الصـرفة والتطـبيقية مجلة جـامعة بـابل للعلـوم الصـرفة والتطـبيقية مجلة جـامعة بـابل للعلـوم الصـرفة والتطـبيقية

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INTRODUCTION

is a semiconducting quaternary compound Copper (Cu), zinc (Zn), tin (Sn), and sulfur (S) that are among the I_2-II-IV-VI aggregates. CZTS may be synthesized by substituting divalent Zn and tetravalent Sn for the trivalent In/Ga element in the kieserite phase[1,2]. A glycoprotein substance called CZTS is utilized in solar cells as a sorbent[3]. The Hall Effect and the Circular Dichroism (CD) are two important techniques used to study the electrical and optical properties of materials, including CZTS (copper zinc tin sulfide). The Hall Effect is a phenomenon discovered by Edwin Hall in 1879. It describes the generation of a voltage difference across a conductor or semiconductor placed in a magnetic field perpendicular to the current flow. The Hall voltage is directly proportional to the product of the applied magnetic field, the current density, and the Hall coefficient of the material. By measuring the Hall voltage and the current, it is possible to determine the carrier concentration and the carrier type (whether it is an electron or a hole) in the material [4]. The Hall Effect provides valuable information about the electrical conductivity, carrier mobility, and charge carrier density of CZTS, which are crucial parameters for understanding its electrical properties and potential applications.

Circular Dichroism (CD), on the other hand, is a spectroscopic technique that measures the differential absorption of left-handed and right-handed circularly polarized light. In CZTS, CD can be used to study the optical properties and chirality of the material. Chirality refers to the property of certain compounds to exhibit different optical behavior for different light polarizations. CD spectroscopy can provide insights into the molecular and electronic structure of CZTS, as well as its interaction with light. It can be used to detect the presence of chiral species, study the symmetry of electronic transitions, and investigate the influence of external factors (such as magnetic fields) on the optical properties of CZTS.Applying the Hall Effect and CD to CZTS can provide important information about both its electrical and optical properties. These techniques contribute to a better understanding of the material's performance and characteristics, aiding in the development and optimization of CZTS-based devices[5].

Experimental

The first part of the discharge chamber contains the target holder, substrate holder, window for laser light passage made of pack quartz, thermal and double valve dump, and is used to prepare thin films of Cu_2ZnSnS_4 of laser energies 700mj by using 200, 250, 300, 350, and 400 pulses. reachable through the discharge rotary and diffusion vacuum, The following is the second segment. For five samples, a YAG laser with a wavelength of 1064 nm and energy (70 mJ) was used. There are 200, 250, 300, 350, 400 (pulses) at a frequency of 6 Hz. Focus the focal lens on the subject. The spacing between distant targets is 2:5 cm. The angle of inclination is around 450. Or The Hall effect (HMS-3000) is being performed on the samples by depositing gold electrodes using an ionic coater and an influenced magnetic field with strength (0.55 Tesla) and power supply (0-2 V) with digital millimeters. .The direct D.C electrical conductivity of the deposited films is measured in the Thin Films Laboratory using a circuit for measuring D.C conductivity that consists of an electrical oven type (Memmert Lab Oven UFB 400,400W) and a

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Keithly model 2400. The sample is placed inside the oven and the temperature is adjusted from the oven control to (373) K. degrees.

RESULTS AND DISCUSSION

- ### The D.C Conductivity and Activation Energy

The electrical conductivity of CZTS films is shown in Figure (1) as a function of temperature for different laser energy (700 mJ) thin films deposited on glass. Conductivity increases with temperature. This seems to be a typical characteristic of a semiconductor feature because of the rising carrier concentration with temperature. in the intrinsic range, the main energy gap. Equation (1), which plots (Ln) vs. the reciprocal of the absolute temperature (10^3/T), may be used to determine the slope of straight lines of (-E/kB), from which we can compute the activation energy. The increase in the conductivity of CZTS compound with the increase in the number of laser pulses can be attributed to a phenomenon called laser-induced doping or laser annealing.When high-intensity laser pulses are incident on a CZTS compound, they can generate free carriers (electrons and holes) within the material through a process called multiphoton absorption. The number of generated free carriers depends on the laser pulse intensity and other factors such as the material's absorption properties.With an increasing number of laser pulses, there is an accumulation of free carriers within the CZTS compound. These additional free carriers contribute to an increase in the charge carrier concentration. As a result, the conductivity of the material increases, as conductivity is directly proportional to the charge carrier concentration .Moreover, high-intensity laser pulses can induce structural changes and modify the local electronic environment of the CZTS compound. This laser-induced doping or annealing effect can lead to a reduction in defects or the activation of previously inactive dopant atoms in the material. These structural changes can have a significant impact on the material's conductivity.It is important to note that the effect of laser pulses on the conductivity of CZTS compound can also depend on other factors such as the laser parameters, the specific composition and purity of the CZTS material, and the quality of the sample preparation. The temperature rise induced by the laser pulses can also play a role in the material's conductivity.In summary, the increase in the number of laser pulses incident on CZTS can result in an increase in the conductivity of the material, mainly due to the generation of additional free carriers and potential laser-induced structural changes or doping effects within the compound [6,7]

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

where:

E_a: is the activation energy.
$\check{T}$: is the absolute temperature.
σ_o: is the minimum electrical conductivity at 0K.

According to Figure (2), there are two phases of conductivity across the warming temperature range. CZTS (Copper Zinc Tin Sulfide) is a quaternary compound semiconductor material that is widely studied for its potential applications in photovoltaic devices. The presence of two activation energies in CZTS is primarily attributed to the existence of two different charge transport mechanisms in the material.

The first activation energy is associated with the conductivity of the CZTS material in the low-temperature range. This low-temperature conductivity is typically dominated by the contribution of intrinsic defects within the crystal structure, such as native point defects or impurities, which result in shallow trap states. These shallow trap states have lower activation energies, which means that they require less energy to be thermally excited, resulting in enhanced electronic conduction. This activation energy is often referred to as the "yellow" activation energy.

The second activation energy, often called the "red" activation energy, is associated with a different charge transport mechanism in CZTS. At higher temperatures, CZTS exhibits a thermally activated behavior due to the presence of deep trap states within the material. These deep trap states have higher activation energies since they require more energy to be thermally excited, leading to reduced electrical conductivity.

When measuring the DC electrical properties of CZTS, researchers often observe a change in the electrical conductivity at certain temperatures. This change can be attributed to the transition from the conduction mechanism dominated by shallow trap states (lower activation energy) to the conduction mechanism dominated by deep trap states (higher activation energy). This temperature-dependent behavior is typically observed as a step-like increase in the electrical conductivity curve.

It is important to note that the specific values of the activation energies and the observed color of the activation energies (yellow or red) can vary depending on the specific CZTS composition, synthesis conditions, and measurement techniques used what the researcher mentioned[8]. Table (1) shows that Ea1 values are less than Ea_2 values. This shows that the conductivity depends on the temperature, since the conductivity is proportional to $T^{3/2}$ [9].

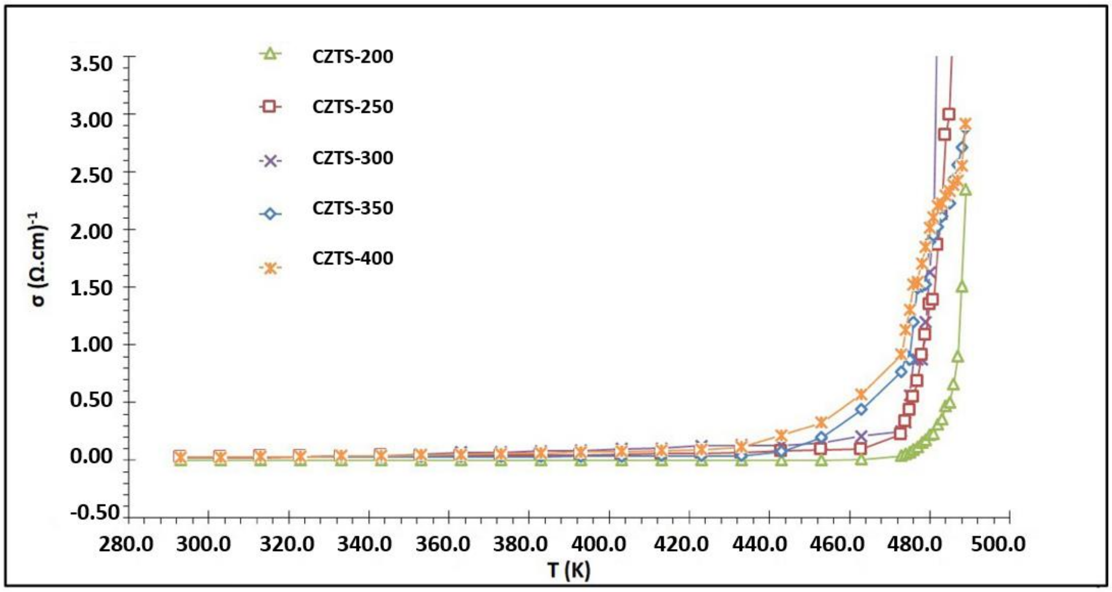

Fig: (1)): The electrical conductivity as a function of temperature for CZTS thin films at different laser pulses.

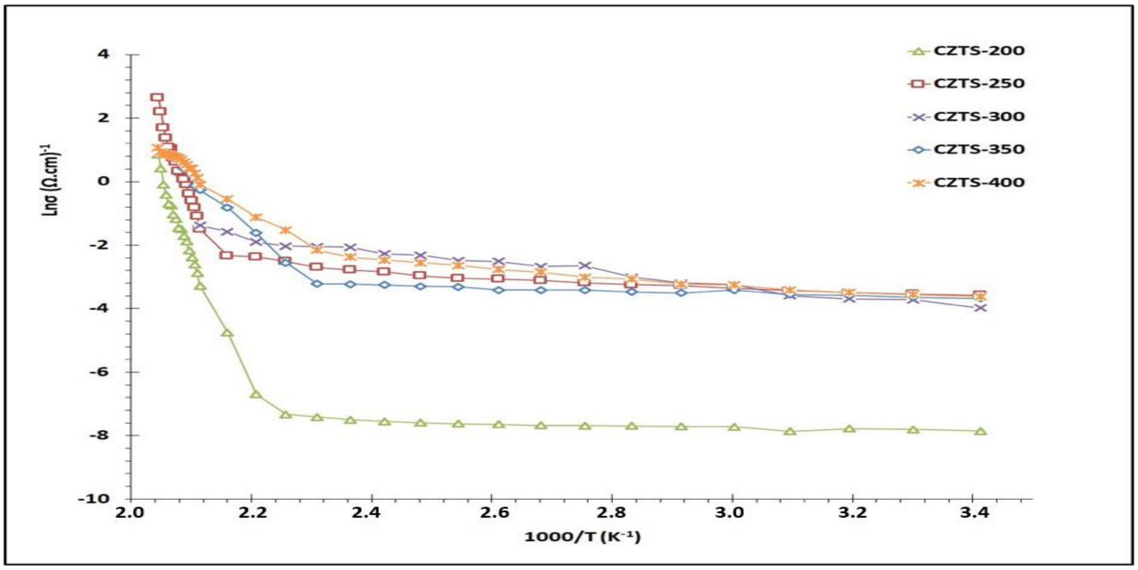

Fig:(2): Lnσ versus 1000/T for CZTS thin films at different laser pulses

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

Sample name	Ea_1 (eV)	Range (K)	Ea_2 (eV)	Range (K)	$\sigma_{R.T}$ $(\Omega.cm)^{-1}*10^3$
$CZTS_{200pules}$	0.032	283-363	3.843	363-473	0.000387912
$CZTS_{250pules}$	0.062	283-363	1.372	363-473	0.02795
$CZTS_{300pules}$	0.156	283-363	1.377	363-473	0.01873
$CZTS_{350pules}$	0.033	283-363	0.369	363-473	0.02537
$CZTS_{400pules}$	0.003	283-363	1.114	363-473	0.02683

- **Hall Effect Measurements**

Knowing the electrical characteristics is essential for calculating the Hall coefficient, RH. The strength of the magnetic field incident on the film and positioned vertically in front of that field determines RH. Hall effect measurements of Cu_2ZnSnS_4 films have been done with lasers of different energies (700 mJ) and with different numbers of pulses. The goal was to find out what kind of charge carriers were present and how concentrated they were. The shift from p-type to n-type conductivity in the CZTS (copper zinc tin sulfide) compound when increasing the number of flashes during the measurement of the Hall effect indicates a change in the majority charge carriers.In the p-type CZTS compound, the majority charge carriers are holes (positively charged). This means that when the external magnetic field is applied perpendicular to the current direction, the majority charge carriers will experience a force that creates a voltage difference perpendicular to both the current and magnetic field, known as the Hall voltage.However, as the number of flashes increases, it indicates an increase in the concentration of free electrons in the CZTS compound. This leads to a transition from p-type to n-type conductivity. In n-type CZTS, the majority charge carriers are electrons (negatively charged) instead of holes.Therefore, the shift from p to n when measuring the Hall effect suggests a change in the dominant charge carriers from holes to electrons due to the increase in the number of flashes. Using a computer program, it can be seen in Table (2) that the conductivity, resistivity, concentration, and Hall coefficient values differ according to the type of carriers (n), but that the mobility values fall as the number of pulses rises.

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

Sample Name	Concentration of Carriers n_H (cm^{-3})	Conductivity $\sigma(\Omega.cm)^{-1}$	Resistivity $\rho(\Omega.cm)$	Mobility $\mu_H(cm^2/V.s)\times 10^2$	Hall Effect $R_H(cm^{-3})$	Type of Carriers
$CZTS_{200\ pules}$	3.16×10^{16}	1.56×10^{1}	0.64102×10^{-1}	3.08×10^{3}	1.98×10^{2}	**p-type**
$CZTS_{250\ pules}$	-7.87×10^{15}	1.81×10^{1}	0.55248×10^{-1}	1.43×10^{4}	-7.93×10^{2}	**n-type**
$CZTS_{300\ pules}$	8.45×10^{16}	4.56×10^{1}	0.21929×10^{-1}	3.36×10^{3}	7.38×10^{1}	**p-type**
$CZTS_{350\ pules}$	-1.02×10^{18}	1.71×10^{2}	0.57471×10^{-1}	1.05×10^{3}	-6.10	**n-type**
$CZTS_{400\ pules}$	1.49×10^{17}	4.12×10^{1}	0.24271×10^{-1}	1.72×10^{3}	4.18×10^{1}	**p-type**

CONCLUSIONS

1- The electrical conductivity has two activation energy values, Ea_1 and Ea_2, due to two types of transfers. The first activation energy is the jump method transition between positional levels within the energy gap, and the second is the thermal stimulation method transition between extended levels.

2- The carrier type of CZTS compound films change from p-type to n-type as the number laser pulses increases, resulting in disparities in carrier density, conductivity, and resistivity. Mobility decreases as laser pulses increase

Conflict of interests.

There are non-conflicts of interest.

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الخلاصة

مقدمة:

تم تحضير أغشية المركب Cu_2ZnSnS_4 الرقيقة باستخدام تقنية الترسيب بالليزر النبضي. استخدم ليزر (Nd–YAG) بطاقة mJ (700) وعدد من النبضات المختلفة وبتردد (6Hz) وطول موجي (1064nm) وضغط (10^{-5}mbar) لترسيب اغشية على ركائز من الزجاج تم دراسة تأثير هول والتوصيلية الكهربائية المستمرة ، وكانت الاغشية من النوع p عند 200 نبضة وتغيرت إلى النوع n مع زيادة عدد النبضات. وأظهرت النتائج طاقتي تنشيط (Ea2, Ea1). وقد وجد أن التوصيلية تزداد مع زيادة عدد النبضات

طرق العمل

تم استخدام ليزر Neodymium–YAG بمدى طاقة ليزر 700 مللي جول وبضغط 10^{-5} مللي بار، وعدد من النبضات بتردد 6 هرتز. تم دراسة تأثير هول والتوصيلية الكهربائية المستمرة.

النتائج

وفقا لدراسة تأثير هول، فإن الأغشية الناتجة المنتجة كانت من النوع p عند 200 نبضة وتغيرت إلى n مع زيادة عدد النبضات يوجد طاقتان للتنشيط (Ea_1 و Ea_2). وقد تبين أن التوصيل الكهربائي يزداد بزيادة عدد النبضات

الاستنتاجات

وجد للتوصيل الكهربائي قيمتي لطاقة التنشيط Ea_1 و Ea_2 . Ea_1هي الانتقال بين المستويات الموضعية داخل فجوة الطاقة التي تحدث بطريقة القفز وطاقة التنشيط. Ea_2 الانتقال بين مستويات أبعد داخل فجوة الطاقة بطريقة التحفيز الحراري .يتحول المركب CZTS من النوع p إلى n عند يزداد نبضات الليزر مما ينتج عنه تفاوتات في كثافة الناقل والتوصيل والمقاومة. تقل الحركة مع زيادة نبضات الليزر.

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