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Comparative Study for solvents effect on Morphological, Optical and Photo-detector Properties of CZTSThin Films

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Abstract. In this work, the effect of solvents on the morphological, optical and photodetector properties of CZTS thin films synthesized by hydrothermal process associated with spin coating technique on glass and silicon substrates at room temperature were investigated.Two different solvents are used such as water (W) and 2-methoxyethanol (2-Me).The prepared films studied using FE-SEM, UV-Vis spectroscopy and I-V measurements. The FE-SEM images shows that the thin film prepared by 2-Me possess uniform structures with spherical shapes. The optical properties results displayedthat optical gap energy for the sample prepared W and 2-Me was equal to 1.81eV and 1.53eV, respectively. At 4 Volt bias, the metal-semiconductor-metal visible photo-detector performance of the CZTS NPs prepared for various solvents was studied under intensity (6 mW/cm^2) at the wavelengths (560 nm) visible light. Photo-detector parameters such as responsivity, sensitivity and detectivity were calculated. Maximum value sensitivity and responsivity for the sample prepared with 2-Me were 204.82 % and 567.9 mA/W, respectively. Moreover, the device revealed short response/ recovery time. Thus, this results revealed that using 2-methoxyethanol as a solvent produces films with better characteristics than using water.

Keywords: Solvents Effect, CZTS, FE-SEM, UV-Vis spectroscopy, Photo-detector.

1. Introduction

The synthesis of chalcopyrite nanocystalline materials with various morphologies is one of the intriguing research areas being investigated due to its promise and potential uses in the magnetic, electrical, optoelectronic, biological domains, and catalytic.[1].

One of the promising chalcopyrite semiconductors is Cu(In,Ga)(S,Se)2. This substance must, however, be replaced with a compound that has the same characteristics as the original material but contains plentiful and low-cost components. CZTS or Cu2ZnSnS4 (copper-zinc-tin-sulfide) is a potential alternative due to its favorable characteristics, which include a high absorption coefficient greater than 104 cm-1 with (p-type) conductivity, an adjustable direct band gap(1.4-1.6eV), strong photostability, abundance, high theoretical conversion efficiency, inexpensive raw material costs and non-toxicity.[2-4].

These characteristics have made CZTS one of the most desirable materials for a variety of applications, including , solar cells [5] , photovoltaic [6], photocatalysis[7], gas sensing [8], photodetectors[9]. The literature survey shows that CZTSnanosturtures can be obtaind by several different techniques, such as nanofibers, wires, nanorods, flower-like, and spherical-like nanoparticles etc[10-14].Among them, hydrothermal method have shown to have greater control over the synthesis of various nanostructures with variable solvents and starting precursors grown on Si substrate was fabricated to investigate their photo-detectors characteristics. Fabrication of the metal-semiconductor-metal(MSM) visible photo-detector device was performed using thermal evaporation deposition of an Al grid using a shadow mask, and The current–voltage (I-V) measurements of the fabricated device were takenutilizing a semi-conductor device analyzer, under visible light of intensity 6 mW/cm^2.

3. Results and discussion

3.1.FE-SEM analysis

Fig. 1 shows the FE- SEM images indicating the effect of different solvents on the surface morphology of prepared CZTS films .The different solvent formed different shaped and sized nano particles(The solvent influenced surface morphology of thin film extensively.), and It is observed that the CZTS nanoparticles prepared in water are inhomogeneous in nature consisting of agglomerated particles with larger grains in the range of 300–500 nm compared to CZTS nanoparticles prepared in 2-methoxyethanolthat possesses uniformin shape and well-dispersed sphere-like nanoparticles with smaller grain size between 30-40 nm.

under moderate circumstances (temperature and reaction time) [15,16].

In this work, we report a comparative study for the effect of solvents(water and 2-methoxyethanol) on morphological and optical properties of Cu2ZnSnS4 Thin Films. moreover, a quick-response MSM visible photodetector was fabricated based on CZTS NPs was grown on silicon substrate and the photodetectors parameters like sensitivity, response and detection are calculated and also reported .

2. Experimental details

Cu_2ZnSnS_4 NPs was prepared in a 100-ml Teflon-lined stainless -steel autoclave via utilizing a simple hydrothermal method. Precursor was prepared by $CuCl_2$, $Zn(CH_3COO)_2.2H_2O$, $SnCl_2{\bullet}2H_2O$, and thiourea (CH_4N_2S) to make a suitable amount in autoclave. This precursor was dissolved in water(30ml) and stirred for one hours to get a yellow solution. Then, the solution was putted into the autoclave and maintained at 220C for seven hours, and then, its cooled to room temperature(RT) naturally. The obtained product were collected by centrifugation and washed via washed with distilled water and absolute ethanol twice before drying in a in vacuum at (80°C) for two hours.to get a Cu_2ZnSnS_4 powder. Finally, the Cu_2ZnSnS_4 powder was dispersed in (15 ml)Water and then deposited by spin coater on the soda lime glass and silicon substrates to prepare thin films. A similar trial was carried out in the 2-methoxyethanol.

Films Morphology and Optical are characterized by a Field Emission Scanning Electron Microscope (FE-SEM, MIRA3 model – TE-SCAN) and UV-Visible- 8001 Spectro-photometer(Meterrech). Devices based on the as-prepared Cu_2ZnSnS_4 film properties of the prepared CZTS films in the wavelength range (300–1100) nm. To obtain detailed information around the energy band gaps of the thin films, an analysis of the dependence of the absorption coefficient on the energy of the photon in the high absorption regions is performed.

The transmittance of the prepared films at different solventare shown in Fig.2 . The spectrum shows low in the ultraviolet region, and high transmittance in the visible and infrared regions, Films prepared with W are more transparent than that prepared with 2-Me, the value of the transmission is about 64% and 32% respectively.

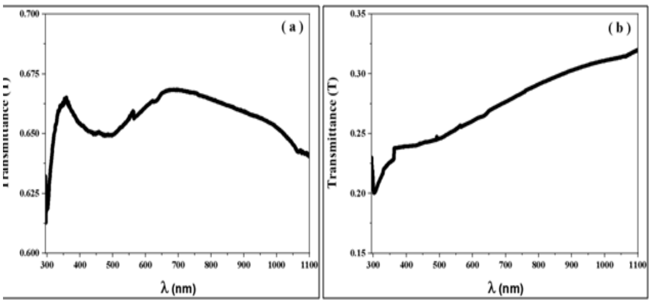

Fig.2. Transmittance for (CZTS) thin films prepared with different solvents: (a) water and (b) 2-methoxyethanol.

The absorption spectra of the CZTS films at different solvent are shown in Fig. 3. These spectra show that the CZTS thin films absorb over the entire visible region of electro-magnetic waves and the tails extend to longer wavelengths.

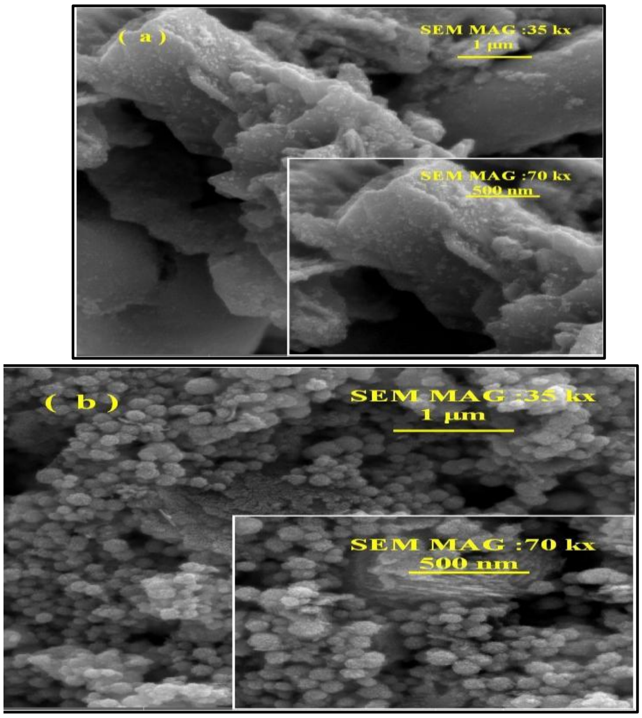

Fig.1. The FE- SEM images for (CZTS) thin films prepared with different solvents: (a) water and (b) 2-methoxyethanol.

However, nanoparticle aggregation has been observed. The importance of a regular surface shape has been widely documented, since agglomeration can minimize grain boundaries [17,18]. It causes an increase in the minority carrier's effective diffusion length, resulting in poor solar cell performance[19]. According to Ali et al. [20], voids can have a negative impact on the electrical and optical characteristics of films.As a result, both voids and agglomeration are undesirable.A dense and well-dispersed surface form was observed for the film prepared using 2-Me as a solvent.As a result, the film prepared with 2-Me as a solvent is regarded the best.

3.2.Optical Properties:

The UV–visible spectrophotometer study was recorded out to explained the optical absorption coefficient($\alpha \geq 10^4 cm^{-1}$) which is conducive to increasing the probability of direct transitions occurrence.

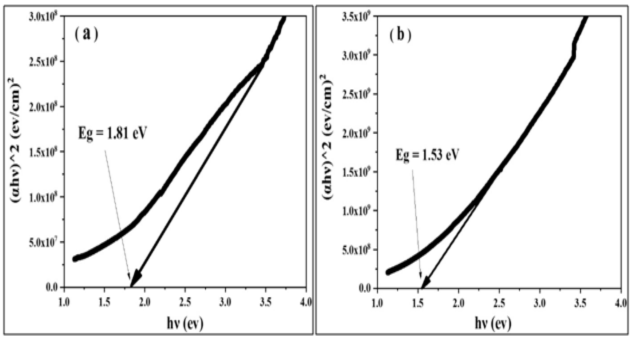

Fig.5. Optical band-gap energy for (CZTS) thin films prepared with different solvents: (a) water and (b) 2-methoxyethanol.

Tauc's plot method[22], was utilized to calculate band gap of CZTS films and is showed in Fig. (45, b). The band gap (Eg) of the deposited films using water and 2-methoxyethanol was noticed to be 1.53 and 1.81 eV, respectively. The obtained values are consistent with the values reported in the literature for Cu_2ZnSnS_4 [23-25]. The variation in band gap can be ascribed to particle size changes as well as changes in the composition of the films, induced by the use of different solvents[26].

3.3.Photo-detector characteristics:

Fig.6 shows the (I-V) curves for the visible sensing of MSM visible photo-detectors based on CZTS NPs grown on Si substrates with various solvents measured under dark and visible light(560 nm) of intensity $6 mW/cm^2$ at -4 and 4 bias voltages. The figure displays that the non-linear behavior, that denotes the formation of a Schottky junction between semiconductor - metal interfaces because the work function of semiconductor (ϕ_S) is greater than the work-function of metal (ϕ_M).

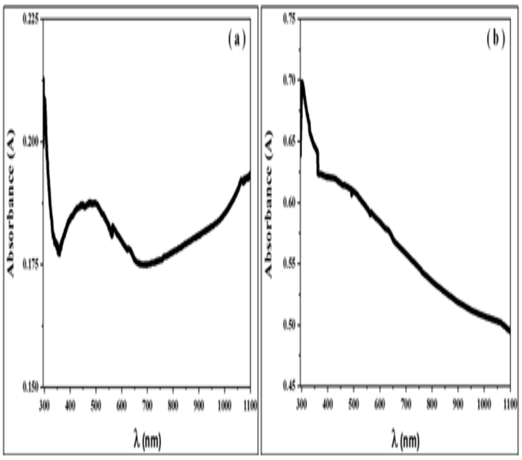

Fig.3. Absorbance for (CZTS) thin films prepared with different solvents: (a) water and (b) 2-methoxyethanol.

By comparing the prepared samples with two types of solvents, it can be noticed that the sample prepared with2-Me has higher absorption in visible region. This behavior can be attributed to the sample's unique shape, which permits incident light to scatter inside its inter space, increasing photon path length and decreasing incident light reflection, i.e., light-trapping effect [21]. As a result, this sample may absorb incident light more effectively.

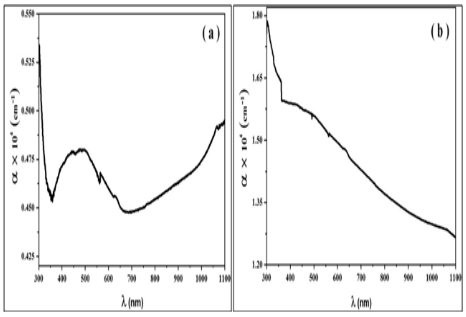

Fig.4. Absorption coefficient for (CZTS) thin films prepared with different solvents: (a) water and (b) 2-methoxyethanol.

Fig. (4a, b) shows the absorption coefficient of CZTS thin films as a function of wavelength, One can evidently see that CZTS thin films have high value of

Where, I_{dark} is the current in the dark, I_{ph} is the difference between current in the light and current in the dark. The magnitudes of photo-sensitivity of all photo-detectors under visible light are recorded in Table 1. From table, it is noticed that the fabricated photo-detectors using 2-methoxyethanol has the highest sensitivity value compared with water as a solvent.The responsivity (R) was determined using the equation below [28]:

$$R = \frac{I_{ph}}{A.P} \text{..............................(2)}$$

Where, P is the light intensity and A is the effective area. The detectivity (D) of was calculated utilizing following equation [29]:

$$D = \frac{R.A^{1/2}}{(2 \times e \times I_{dark})^{1/2}} \times 100 \text{ ....(3)}$$

Where, e is the electron charge. The magnitudes of responsivity and detectivity of the fabricated photo-detectors under visible light are recorded in Table 1. In addition, it is noticed that The responsivity values are higher than others reported[30,31].

The response and recovery times of the MSM photo-detector were calculated for one cycle of the current-time pulse schemes revealed in Fig. 6. The response time (time the time required for the photo-current to grow from 10% to 90% of its saturation value) and recovery time (the time needed for the photo-current to drop from 90% to 10% of its saturation value) for the devices were noted to be < 1 sec, as displayed in in Table 1, higher than others reported[32]. The quick response in this paper indicates that the (Al/CZTS NPs/Al) MSM-structured visible detector could be utilized in practical applications.

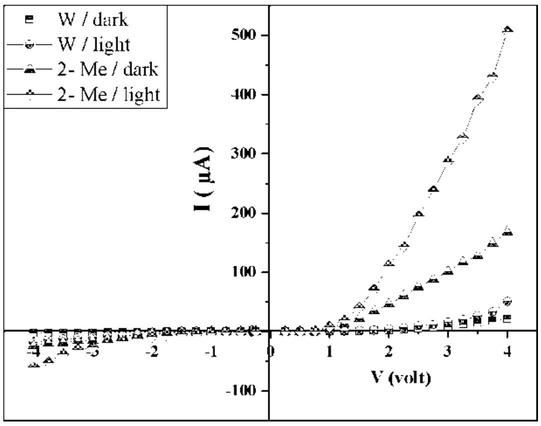

Fig.6. I-V characteristics of CZTS thin films with and without light.

The photo-response of the fabricated photode-tectors was measured at a bias voltage of 4, with an ON and OFF cycle (30 s) under visible light as display in Fig.6. All curves displayed rectangular formed profiles, and photocurrent magnitudes for each ON/OFF cycle were constant and reproducible. In addition, the current magnitude increases By using two different solvents that can be obviously seen of the current-time pulse schemes.

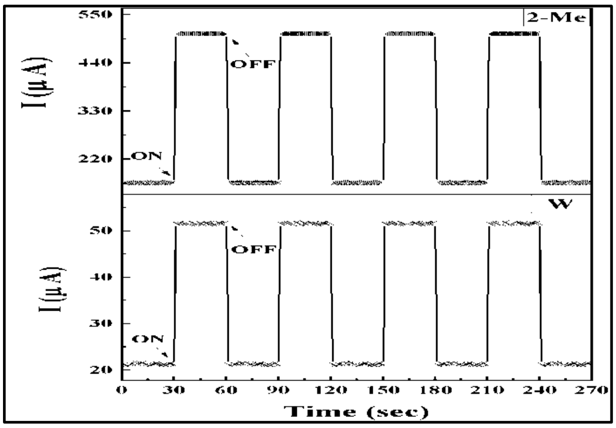

Fig.7. I-T measurements of CZTS thin films with different solvents under light .

The photo-sensitivity (S) of photo-detector was calculated utilizing following equation [27]:

$$S(\%) = \frac{I_{ph}}{I_{dark}} \times 100 \text{ ....(1)}$$

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Table 1. The response, recovery times and sensitivity, responsivity and detectivity for CZTS thin films with different solvents.

Solvent	Rise Time (sec)	Fall Time (sec)	S %	R (mA/W)	D^*10^9 (Jones)
water	0.79	0.8	142.86	57.2	8.51
2-methoxy ethanol	0.8	0.8	204.82	567.9	30.03

4. Conclusions

We synthesized CZTS NPs thin films by hydrothermal process associated with spin coating technique on glass and silicon substrates using two kinds of solvents (water and 2-methoxyethnol) .the FE- SEM images indicate , Compared to water solvent, reduced void defects and better surface roughness are observed using 2-meth solvent, attributable to different vaporization tendency of constituents in the solutions.The band gap of the samples for 2-Me and W was calculated as 1.53eV and 1.81eV, which is in the range of optimal band gap value for absorber layer in the photovoltaic cells.Photo-detector characteristics indicated that the MSM photodetector had good stabilization, a big photo-current, high sensitivity, and premium responsivity when illuminated at 560 nm at light intensity (6 mW/cm2) with 4 V bias voltages. Moreover, the device revealed short response/ recovery time. These findings indicate that the manufactured photodetectors are a promising choice for optoelectronic applications.

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دراسةمقارنةلتأثيرالمذيباتعلىالخصائصالمورفولوجية ، البصرية و الكاشف الضوئي لأغشيةCZTSالرقيقة

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الخلاصة: في هذا العمل، تم دراسة تأثير المذيبات على الخواص المورفولوجية والبصرية والكاشف الضوئي للأغشية CZTS الرقيقةالمحضرة بطريقة الحرارية–المائية المرتبطة بتقنية الطلاء الدوراني على قواعد من الزجاج والسيليكون في درجة حرارة الغرفة. تم استخدام نوعين مختلفين من المذيبات وهي الماء و 2–ميثوكسي ايثانول. كما تم فحص الاغشية المحضرة بواسطة مجهر الالكتروني الماسح للمجال الباعث، طيف الامتصاص المرئية/فوق البنفسجية و قياسات تيار– فولتية . اظهرت صورالمجهر الالكتروني الماسح للمجال الباعث أن الغشاء الرقيق المحضر بواسطة 2–ميثوكسي ايثانول يمتلك تركيب منتظم ذات شكل كروي. أوضحت نتائج الخواص البصرية أن فجوة طاقة البصرية للعينة المحضرة بالماء و 2–ميثوكسي ايثانولكانت تساوي 1.81 eV و 1.53 eVعلى التوالي.عند تحيز 4 فولت، تم فحص أداء الكاشف معدن–شبه موصل–معدن لجسيمات CZTS النانوية المحضرة بمذيبات مختلفة تحت اشعة المرئية ذات شدة 6 mW/cm^2 عند طول موجي 560 nm. وقد تم حساب معلمات الكاشف الضوئي مثل الاستجابة ، التحسسية و الكشفية. اعلى قيمة للتحسسية و الاستجابة كانت للعينة المحضرة باستخدام 2–ميثوكسي ايثانول كانت 204.82 % و 567.9 mA/W على التوالي . علاوة على ذلك ، كشف الجهاز عن وقت استجابة / رجوع قصير. وبالتالي اشارت هذه النتائج ان استخدام 2–ميثوكسي إيثانول كمذيب ينتج أغشية ذات خصائص أفضل من استخدام الماء.