Effect of Laser annealing on structural and thermoelectric properties of SnSe thin films
SUHA H. IBRAHEEM,

dr.suhad@uomustonsiriyah.edu.iq.
07814085403
College of Basic Education, Mustansiriyah University, Baghdad-Iraq

Abstract:

In this study, flash evaporation technique was adopted to prepare SnSe thin films onto glass substrates kept at room temperature. The effect of CO_2 laser annealing on the structural properties and thermoelectric characterizations of SnSe films was investigated in power annealing (10 W) at (10,15,20 Min). Morphologies and structures of the crystalline were determined using atomic force microscope and X-ray diffraction. Power factor, electrical conductivity, and the Seebeck coefficients, were determined. The results demonstrated that the power factor and the Seebeck coefficient were enhanced as the annealing time increased. When the annealing time reach to twenty minutes at 500K, the power factor and Seebeck coefficient of SnSe thin films were found to be about 6.33 µW/cm.K^2 and 650 µV/K., respectively.

Keyword: *flash evaporation technique, Tin Selenide, structural properties, electrical properties, and thermoelectric properties.*

1. **Introduction***:*

SnSe has recently gained much attention owing to their unique structural properties and show good thermoelectric (TE) properties [1,2]. As well, it have drawn a great deal of interest it, exhibit chemical stability and nontoxic and economical earth-abundant elements [3]. SnSe are part of orthorhombic crystal structure and its parameter of the unit cell was a= 1.149nm,b=0.415nm and c=0.444nm [4,5]. In order to optimize the thermoelectric properties of Tin Selenide (SnSe) thin film, many studies have been performed to prepare SnSe thin films from various experimental techniques [6–12]. Among all growing methods, vacuum thermal method is important because of its very simple and low cost. Song et al.[13] have reported that the thermoelectric property of SnSe thin films was enhanced by thermal annealing. Laser annealing (LA) is a promising industrial of the laser applications and submitted to substitute for traditional thermal annealing in

present time[14], where used different types of lasers with various wavelengths including such as CO2 laser that studied by using a small power with the effective consumption are suitable for the annealing[15].

In the present study adoption of carbon dioxide laser for anneal (SnSe) films are produced by flash evaporation methods, and effect of laser annealing on the thermoelectric and structural properties of SnSe thin films.

2. Experimental

High purity SnSe powder (99.999%) was used to syntheses thin film by flash evaporation method on the glass at 298 K. the vacuum system model (Edward 306A) are used for the films evaporation. The flat glass are treated by ultrasonic waves, acetone, DW then submitted to the air by the blower.

The powder is put in the heated boat from the feed by passing into the guide funnel, depending on the manual vibrating handmade system. Increasing of the temperature of the boat to 1500K for evaporating SnSe. The used vacuum for the powder at less than 10^{-5} Torr in the pressure at 298 K inside the vacuum. The distance was 15 cm between the source and substrate. Then, the films were exposed to the surrounding atmosphere. After that the prepared thin films were annealing by using CW- CO_2 laser device of type (engraving machine) with a maximum power of 50W with the wavelength of 10,6 µm. Moreover, the power annealing 10W at (10, 15, 20 min) at 50cm distance between the sample and laser. The laser beam was focused using a lens with a focal length of 20 cm. the laser spot of the sample was (0.5 cm). X-ray diffraction (XRD-6000, Shimadzu, made in Japan) are done using Cu-Kα (λ=1.54) for provides data that related with the film. The film thickness was estimated by the weighting technique and approximately120 nm. The microstructure and surface morphology analysis of these films were studied using Atomic Force Microscopy and (Scanning probe Microscope type (AA3000),supplied by Angstrom Advanced Inc. ;HMS-3000).Seebeck coefficient was determined at a temperature range from 300 to 800K.This is done by making one end of the film cold at a temperature of T1 while the second end is heated to a temperature of T2 and a thermocouple is installed on it to measure the temperature while recording the voltage generated (ΔV) as a result of the thermal gradient between the two ends of the film , Where the Seebeck coefficient is defined as the ratio of the Seebeck voltage (ΔV) across the films with respect to the temperature difference (ΔT). Keithly model 616.Was used to determine the electrical conductivity includes studying the variation of resistivity with temperature range (300-800) K.

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Thermal conductivities of SnSe films were measured using the two-wire differential 3ω method [16].

3. Results and discussion:

The XRD patterns of our SnSe films annealed by laser with different periods are shown in Fig.1.The XRD pattern shows worthwhile to observe that the predominant peaks is (111). The samples peaks match JCPDS 32-1382 that belong to orthorhombic phase. Our results come agreement with kumar et al.[17] and Zainal et al. [18] with preferred orientation of (111) plane for the SnSe films accumulate on the vacuum evaporation method. As laser annealing the films, the peaks change to be sharper and narrower with the long time of laser annealing. Moreover, some small peaks with different orientation were observed after annealing. The sharp peaks was showed to (201), (011), (111), (400), (311) , (411),(020), (511).(321) and (420) planes of SnSe. The peaks are stable with the orthorhombic SnSe peaks that found by papers that synthesized by many methods [19].
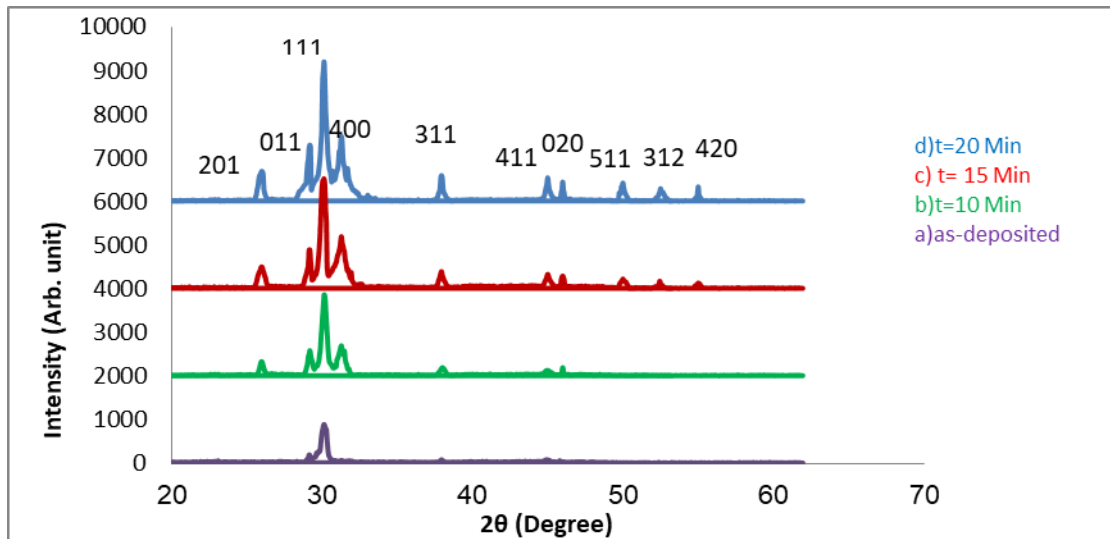

Fig.1. X-ray diffraction scheme of the SnSe thin films as deposited and annealed by laser for (10 min), (15 min), and (20 min)

The obtained results for the morphology of the surface films by AFM images, Fig.(2) demonstrated three dimensions pictures of SnSe before and after annealing by laser .It was noticed that film surfaces are uniformity crystalline and homogeneity superficial good. Also the result showed that when increase the duration of laser annealing, some types of crystal defects was reduce gradually, which make films surfaces form more regularly[20]. In addition, increasing particle size, as well as surface roughness and RMS as list in Table 1.
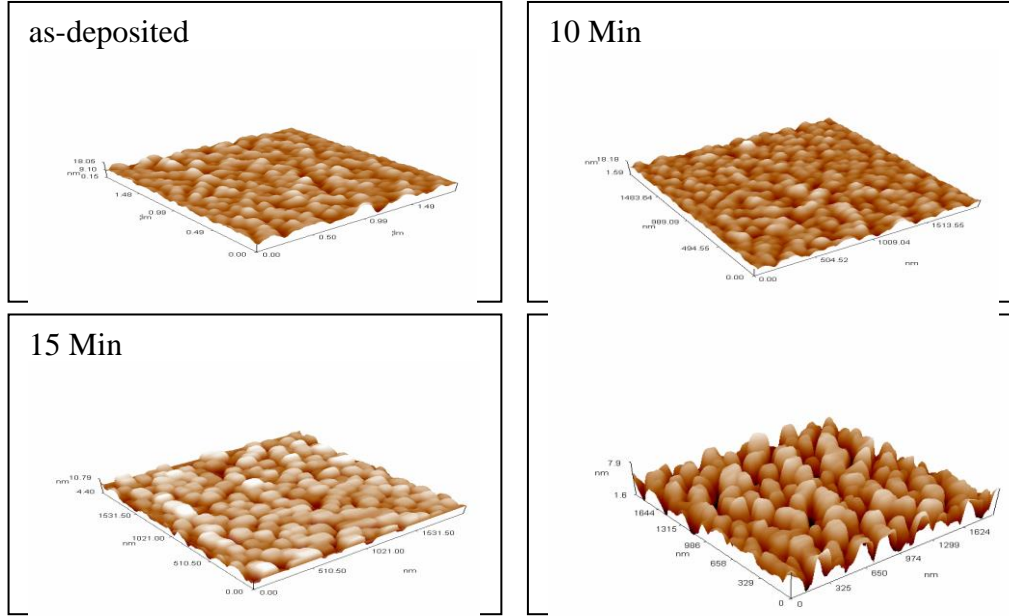
Fig. 2. SnSe Surface topography as-deposited and under different time of annealing by laser

Table 1.AFM analysis of SnSe thin films under various time of annealing by laser

Annealing time (min)	Average Roughness (nm)		RMS (nm)	Average Grain Size (nm)
As-deposited	0.55	0.43		40.83
t=10	0.89	0.87		60.47
t=15	1.12	1.91		71.64
t= 20	1.58	2.31		86.28

Thermoelectric materials can convert thermal energy to electric energy, referred to as "thermoelectric generation", the main topic in the research is improving thermoelectric performance of SnSe by laser annealing, TE materials efficiency is determine by dimensionless figure of merit, and TE power factor as expressed equation (1),[21]

$$ZT = \sigma S^2 T / K, \qquad (1)$$

Where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity is absolute temperature. Properties of the electrical transport as a function of temperature were performed on the samples as deposited and laser annealing with different times, as shown in Fig.3, involved Seebeck coefficient, thermal conductivity, power factor, electrical conductivity, and dimensionless figure of merit (ZT). Fig.3(a) shows the trend of the Seebeck coefficient varying with the temperature. The Seebeck coefficient of all values are positive, which indicates that these SnSe films are the p-type material [22]. In addition, obviously, the Seebeck coefficient increases at the beginning, then reaches a maximum value at 500 K, which is 550.6 μV/K for the films as deposited , and then decrease at temperatures over 500K. This behavior might be attributed to the increasing carrier concentration at high temperature by thermal excitation [23] ,whereas Seebeck coefficients are inversely proportional to carrier concentrations.; while simultaneously the electrical and thermal conductivity increase at a temperature of 500 K, as shown in the Fig.3(b) and Fig.3(c). Similar result have been reported by Heo et.al. [24]. After laser annealing the Seebeck coefficients are increased compared with that before annealing. This occurs as a result of the decrease in defects with the increase in the annealing time, which leads to a decrease in the carrier degree and an increase in the Seebeck coefficient. Seebeck coefficient. Seebeck coefficient shows a maximum of 650 μV/K when the sample annealed at 500K for 20 min. Fig.3(b) shows the effect of laser annealing on the electrical conductivity of thin films for different time. It can see that when increasing time of annealing the electrical conductivity decreased. This is due that the electrical conductivity are directly related to the carrier concentration and mobility. Period of the annealing become high at 20 minutes, with increasing of the electrical conductivity. Achieving of the highest electrical conductivity at 800K was 27.5 $S\,cm^{-1}$. The thermal conductivity are reduce from 1.1 to 0.7 W/(m·K) were shown by other researchers [25]. The power factor is determines as thermoelectric converter. It was measured depending on the electrical conductivity and the Seebeck coefficient (S^2 σ). Fig. 3(d) demonstrated the power factors for annealing SnSe with laser at many periods. The top power factor at 500 K was 6.33 $μW/cm.K^2$ by annealing for twenty minute. The enhancement of power factor is mainly contributed by the increase of Seebeck coefficient. This power factor which is higher than value of SnSe thin films in the literature by Burton et.al. [26] and Yuyu Feng et.al.[27]. Furthermore, the estimated ZT value with the calculated thermal conductivities of SnSe films Fig.3(e) seems

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to increase with the increasing annealing time. However, due to the enhancement of the power factor. The maximum ZT value of 0.67 was achieved for the film annealed for 20 Min at 500 K. our results showed that this value is the highest value that found in SnSe films.
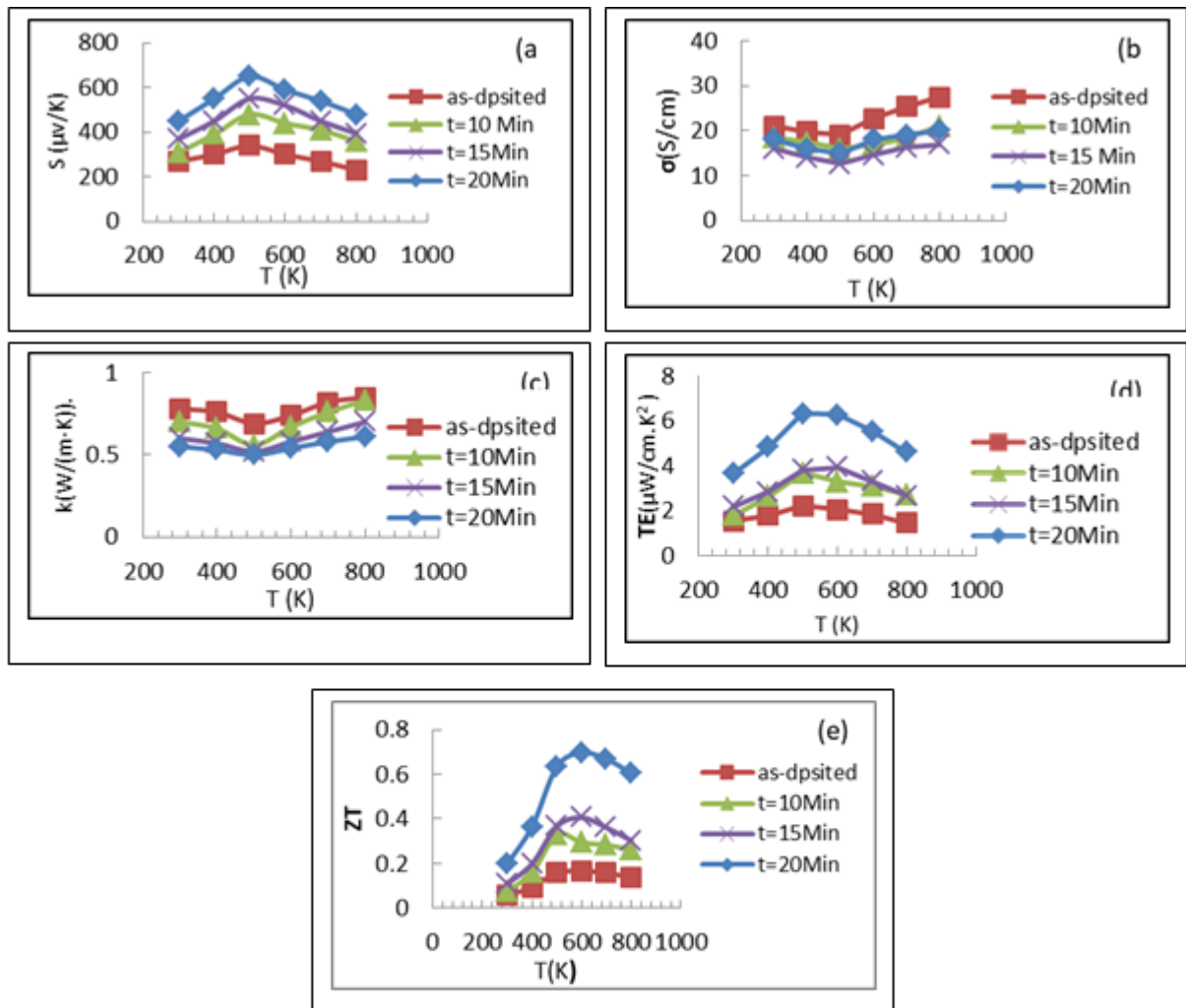

Figure3. SnSe, thermoelectric properties as a function of temperature. (a) Seebeck coefficient. (b) Electrical conductivity. (c) Thermal conductivity. (d) power factors. (e) ZT values.

4. Conclusion

This study signifies the importance of laser annealing parameters, such as temperature and time, on the thermoelectric properties of SnSe thin films. The X-ray diffraction studies revealed that all the samples are polycrystalline in in nature having preferred orientation in (111) direction. The morphological of the surfaces films are uniformity crystalline and homogeneity superficial good and increase particle size when increasing the duration of laser annealing. Electrical conductivity and Seebeck coefficient were measured. When the annealing samples with laser, the power factors was enhance. The maximum power factor of 6.33 μW/cm.K^2 achieved at 500 K by annealing for 20 Min for annealing SnSe

Acknowledgments

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تأثير التلدين بالليزر على الخصائص التركيبية والكهروحرارية لأغشية SnSe

أ.م.د.سهى حسين ابراهيم

dr.suhad@uomustonsiriyah.edu.iq

موبايل: 07814085403

كلية التربية الاساسية – الجامعة المستنصرية – بغداد – العراق

مستخلص البحث:

في هذه الدراسة ، تم اعتماد تقنية التبخير الومضي لتحضير أغشية SnSe الرقيقة على ركائز زجاجية محفوظة في درجة حرارة الغرفة. تم دراسة تأثير التلدين بليزر ثاني أكسيد الكربون على الخواص التركيبية والخصائص الكهروحرارية لأغشية SnSe في التلدين بالقدرة (10 وات) عند (10 ، 15 ، 20 دقيقة). تم تحديد أشكال وتركيب البلورات باستخدام مجهر القوة الذرية وحيود الأشعة السينية ، كما تم تحديد معامل القدرة ، والتوصيل الكهربائي ، ومعاملات سيبيك. أظهرت النتائج أن معامل القدرة ومعامل سيبك قد تم تعزيزهما مع زيادة زمن التلدين. عندما يصل وقت التلدين إلى عشرين دقيقة عند 500 كلفن ، وجد أن معامل القدرة ومعامل سيبيك للأغشية الرقيقة SnSe يقارب μW/cm.K 6.33 و μV/K 650 ، على التوالى.

الكلمات المفتاحية: تقنية التبخير الومضي ، سيلينيد القصدير ، الخواص التركيبية ، الخواص الكهربائية ، الخواص الكهروحرارية.