

The Influence of Temperature on the structural and optical properties of Sb₂S₃ thin films prepared by chemical bath deposition method

Niran F. Abdul-Jabbar¹, Raid A. Ismail², Mustafa W. Fatehi¹

¹ Physics Department, College of Education for Pure Sciences, Tikrit University, Tikrit, Iraq

² Physics Department, College of Science, University of Technology, Baghdad, Iraq

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Corresponding Author:

Name: Mustafa W. Fatehi

E-mail: mwathiq84@gmail.com

Tel:

Introduction

Scientists and researchers have been interested in studying semiconductor materials since the beginning of the 19th century, because these materials have distinct electrical properties where semi-conductor materials behave as insulators at low temperatures, while Good electrical conductivity at high temperatures shows that the behavior of semiconductors is varied. Magnetic and electromagnetic fields make it the basic structure of this electronic technology [1,2]. Thin films are used in the manufacture of electronic devices and optical coatings, etc. . The main properties of thin films such as film thickness, film composition, crystal orientation, etc. depend on deposition conditions [3]. Semiconductor materials have different fields. Between 1940 and 1950, a revolution began. The electronics industry is powered by the transistor and then the micro-electronic circuits, the main reason for this. The sudden change is due to the possibility of preparing pure semiconductors [4]. Among these semiconductors are antimony sulfide. The researchers were interested in antimony Sb₂S₃ and attracted special attention, because it has Good optical properties, High thermal energy, good spectral response [5,7]. The properties of Sb₂S₃ antimony sulfide are mostly determined by their crystal composition, size and morphology, so the installation

ABSTRACT

In this study we used chemical bath deposition method for deposited Sb₂S₃ thin films on glass substrate. The study analyzed the optical properties and structural characterization of Sb₂S₃ thin films. The structural properties were studied on the thin films by x-ray diffraction (XRD), Scanning electron microscope (SEM), Energy dispersive X ray Analysis (EDAX). The XRD pattern showed that the thin films were polycrystalline, and EDAX showed that the constituents of the element were found to be chemically balanced and convergent peak (ie, verification chemical balance of phase Sb₂S₃). The optical properties showed that the optical energy gap at 40°C is 2.8 eV, and at 50 °C is 2.6 eV, and the optical transmittance at 40°C is %80, and at 50°C is reached about %60.

of Sb₂S₃ material of the size and shape controlled by being important of applications, and from These applications which include thermoelectric cooling devices, resonant laser cavity, and optical data storage devices [8,10], and has a negative electric conductivity of type (n-type) [11]. Semiconductor sulphide antimony belongs to the group (V-VI) of the periodic table, and antimony Sb₂S₃ is obtained through various techniques such as chemical bath deposition, chemical thermal spraying, successive ion layer, reaction method, and material entering into Configuration Sb₂S₃ is universally available and inexpensive [12].

Experimental part

Thin films were prepared on Corning substrates with thickness (0.1 mm) and area (2.5 × 3.5) cm² German origin, and the reason to choose this kind of glass substrate back to endurance. High temperatures that reduce internal stresses of the deposition film during deposition process especially at high and low temperature sequentially. The glass substrate were washed with normal water and then cleaned with a fine glaze and a glass cleaner and well washed to remove fat and lingering dirt on the surface of the glass substrate. Finally, wash thoroughly with distilled water and then put in the oven for drying (15 min) and temperature at 80°C. After cleaning the

selected glass substrate for the purpose of deposition, the weight is measured using a balance Sensitive type (Mettler. A.E_160) Sensitivity (10^{-4} gm) and its capacity (120gm) After the completion of the deposition process thin films the base weight was calculated to determine the weight difference between the two cases (Δm), for the thickness of the film can be measured using the following relationship[13]:

$$t = m / \rho A \dots (1)$$

Where ρ : is Compound density (g/cm^3).

t: is thickness of the film (cm).

m: is the mass of the film deposited on the substrate (g).

A: is the area of the deposited films(cm^2).

The solution used in the preparation of Sb_2S_3 films of SbCl_3 antimony trioxide was prepared. It is a chemical compound in the form of soft, colorless crystals, easily attached to contact with air and Molecular weight (266.53 g/mol) and with purity (99.9 %), The solution was prepared at a molecular concentration of (1 mol/L) The following relationship was used to calculate the required weight[14]:

$$W_t = M \cdot M_w \cdot 1000 / V \dots (2)$$

Where V: Is the volume(ml)

M_w : Molecular weight (g / mol)

W_t : The weight of the material(g)

M: molar (mol/l)

The materials weight can be calculated by using a sensitive balance (Mettle AE_160) with sensitivity (10^{-4} gm) and its capacity (120 gm), then dissolve the material in (10 ml) of acetone, and mix the solution prepared by mixture (hot and stirrer) for 10 min. And then left until the preparation of the second solution, prepared the sodium thiosulphate and its chemical formula ($\text{Na}_2\text{S}_2\text{O}_3$), which are white crystals highly soluble in water with a molecular weight of (158.09 g /mol) and a purity of (99.9%) and used the relationship(2) to get the desired weight. The material is then melted in a baker containing (65 ml) distilled water and also mixed for 10 minutes, Then mix these solutions with each other using the Hot and Stirrer mixer for up to 1 min so that the solution is well mixed and homogenous, After completion of preparation of the solution to be deposited on the glass substrate we are deposition process, Add drops of Tartaric acid ethyldiamine (EDTA) to maintain acid pH function pH 2.3, where the glass substrate is placed in a glass container (Baker) capacity (50 ml) is empty and then put the container which contains the glass substrate on the hot and Stirrer mixer, and pour the solution until it is submerged The entire glass substrate is placed vertically on the vessel walls, During the deposition process, the gradual change in the color of the solution is observed, is changed from colorless to yellow, then orange, and finally turns red. After the deposition process is completed, we get the thin films to be tested and the films are placed in the oven at 100°C for 15 min, and become ready for measurement. Specification of the devices and type they are microscope electron microscopy analyzes is

(TESCAN, Vega III, Czech Republic), spectral optical analyzes is (UV VIS.NIR, Jasco, V670, Japan), x-ray diffraction is oxford Instruments, Twin-X , UNITED KINGDOM.

Result and Dissection

Growth kinetic: Chemical reaction can be controlled by controlling various deposition conditions, and mechanical Growth of thin films prepared varies from film to film and from deposition to another, The change in chemical bath conditions affect on the thickness of the thin films, as well as the absence of deposition of certain conditions may be due to ions that did not have enough time to reach the surface of the glass substrate, And thus settle at the bottom of the vessel glass, or on its walls, which negatively affects the thickness of thin films. The behavior of thickness versus deposition temperature is shown in Fig.1. It shows the effect of deposition temperature ($40\text{--}70^\circ\text{C}$) on thickness thin film Sb_2S_3 , when increasing the deposition temperature until reaching to 60°C the thickness of the films increase because of the large number of ions on the surface of the glass substrate leading to grain growth and increase thickness of the film, after this temperature the thickness of film decreasing by increasing temperature.[15]

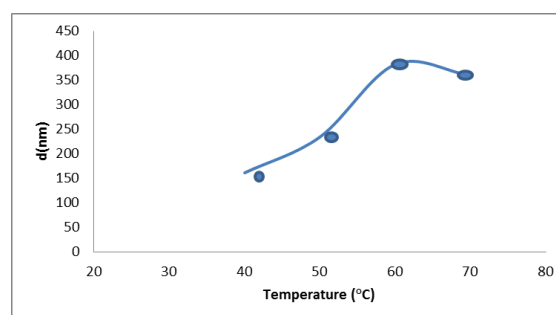


Fig.1: The thickness of thin film against deposited temperature

Structural properties:

Figure (2) represents the X-ray spectrum of the Sb_2S_3 thin films using the bath deposition method at different deposition temperatures (40, 50) $^\circ\text{C}$, we observe through the figure that X-ray diffraction spectra for different temperatures of Sb_2S_3 thin film that predominate crystalline orientation are 020 at (2θ) 16.41° , 16.43° , 16.40° and 16.37° respectively with directions Other crystals are 101, 221 and 331, which show that the compositions are polycrystalline and type orthorhombic for thin films Sb_2S_3 , when corresponding with ICDD Card (JCPD file no. 6-0474), the also observes through the figure that the two spectra which represent the thin films Sb_2S_3 that deposited at different temperature(40,50) $^\circ\text{C}$, shows an increase in the deposition temperature produces in increased in the X-ray due to increase thickness of the thin film and improved compositions crystalline film. This result at precipitation temperatures is consistent with the results of Sb_2S_3 thin films Prepared by

chemical deposition method obtained by researchers [16].

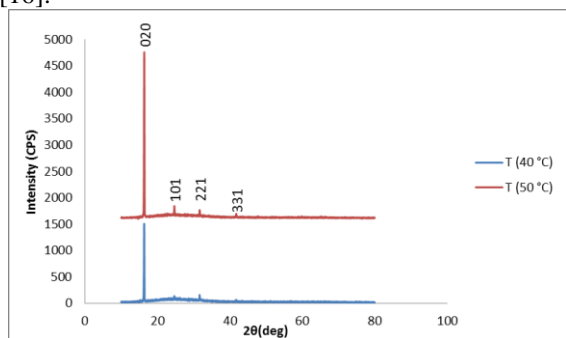


Fig. 2: X-ray diffraction of Sb₂S₃ thin films at(40,50) °C.

The lattice constant a, b and c for orthorhombic structure are calculated using the following relation[17] :

$$(1/d^2) = (h^2/a^2+k^2/b^2+l^2/c^2) \dots\dots(3)$$

The lattice parameters was found to be a =11.425 Å, b =10.2920 Å and c =3.660 Å, which are in good agreement with the standard value [18]. The average particle size is calculated from the diffraction peak broadening from the peak (020) by using Debye Scherer equation [19] :

$$D = 0.9\lambda / \beta \cos\theta \dots\dots(4)$$

Where λ is the wavelength of XRD patterns which equal to 0.154 Å, β is the full width at half maximum (FWHM),0.9 is a numerical constant called Scherer' constant and θ is the Bragg diffraction angle in degrees.

The average particle size was found to be 161.56 nm.

Morphological and compositional Study:

The scanning electron microscopy of Sb₂S₃ thin film at deposition temperature 50°C shown in (Fig.3). Spherical and bunches of thread like structure was observed. The spherical grains are fused with each other. It well covers the glass substrates. The figure illustrates that randomly distributed of threads.

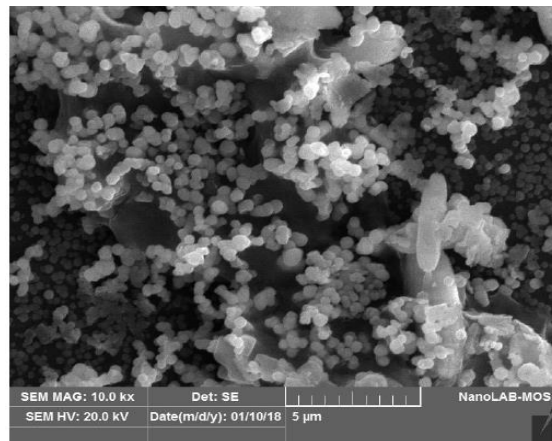


Fig.3:Scanning electron microscopy of Sb₂S₃ thin films at deposition temperature 50°C.

Quantitative analysis of the film was carried out using the EDAX technique for Sb₂S₃ at 50 °C to study the composition in the film.

Fig.4 illustrates a typical EDAX pattern of Sb₂S₃ thin films. Through the shape we notice the emergence of some peaks such as aluminum and silicon and the reason for this back to the glass substrate, This is consistent with the published results and the source [20].

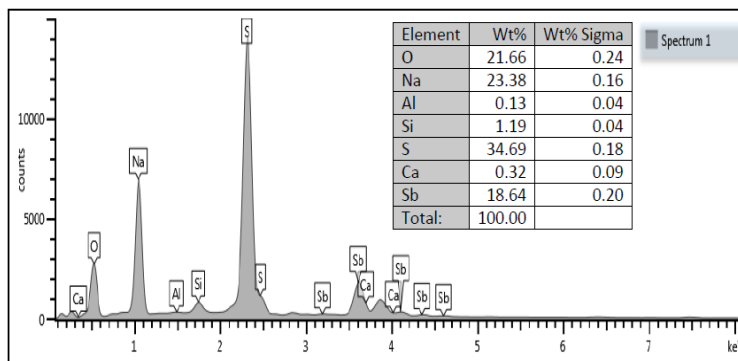


Fig4.: The EDAX is curved to the Sb₂S₃ film at deposition temperature 50°C

Optical Properties:

1-Absorption Coefficient

The Absorption Coefficient can be calculated from the following relation[21]:

$$\alpha = 2.303 A / t \dots\dots\dots (5)$$

where (t) is the sample thickness, (A) is the absorbance, it can be calculated from the relationship:

$$A = \log I_0 / I \dots\dots\dots(6)$$

Fig. 5 illustrates the absorption coefficient spectra of Sb₂S₃ thin films at deposition temperature (40,50)°C in the wavelength range of (300-900) nm, The absorption spectra were used to calculate band gap,

type of optical transition and absorption coefficient, etc. The study show that the presences of absorption edge of exponential shape, It is due to homogeneity of the films and normal band structure. The spectra shows two regions, one for higher wavelength with practically lower absorption and other for lower wavelength in which absorption increases steeply. Where there is a clear increase observed in the absorption coefficient at energies greater than 2.9 eV. This sudden increase in the absorption coefficient sharply shows that the transitions arising from the basic absorption process are direct transitions, In addition, the study suggested notice from the shape

when the deposition temperature increases the value of the absorption coefficient decreases because the temperature increases the crystallization of the material that reduces the crystalline defects as well as the non-absorption of atoms because of high transmittance [22].

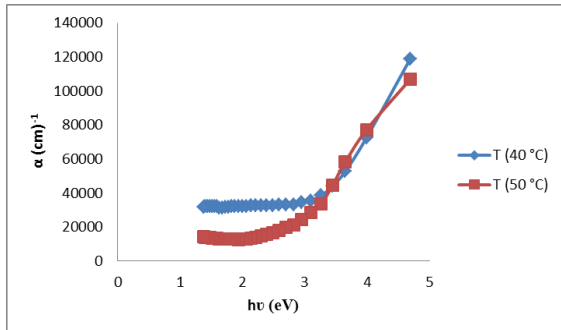


Fig5. Effect of temperature (40,50) ° C in the absorption coefficient.

2- Optical Transmission:

The spectrum of optical transmittance is influenced by many factors. The most important of these factors is the photon energy and structure chemical composition, crystalline structure, film thickness and surface topography of the film. Fig. (6) shows that transmittance is reduced with high deposition temperature from (40 to 50) °C, The high temperature helps to produce ions and reshape deposit that have a role in the composition of the thin film, In addition to providing kinetic energy interaction which in turn perform to increase the collisions between negative and positive ions in the solution, leading to an increase in the number of atoms deposited On the surface of the glass substrate and thus an increase in granular particle size, thereby raising in thickness of the film.

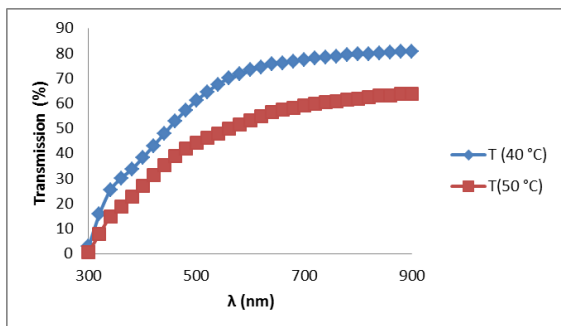


Fig 6. Effect of deposition temperatures(40,50) °C in the transmittance spectrum of Sb₂S₃ film.

The transmittance values above correspond with results published for Sb₂S₃ films in chemical bath deposition [23].

3- Optical Energy Gap (E_g):

The optical energy gap can be defined as the energy needed to transfer the electron from the peak of

References

[1] Sirotin, Y. and Shaskolskaya, M. (1982). Fundamentals of Crystal physics. Mir publishers, Moscow,.

valence band to the bottom of the conduction band, which has been called forbidden due to the instability of the electrons in semiconductors .The value of the energy gap depends on the distribution and arrangement of the atoms in the crystalline structure, the energy gap can be calculated from the relation [24]:

$$(ah\nu) = B (h\nu - E_g)^r \dots\dots\dots (6)$$

where (E_g) is the optical band gap, (hν) is the energy of the incident photon, (B) the absorption edge width parameter and (r) the exponent depends upon the type of optical transitions in the material , where r = 1/2 for Direct allowed transition , r = 3/2 for Direct forbidden transition , r = 2 for Indirect transition allowed and r = 3 for Indirect forbidden transition.

Sb₂S₃ thin films prepared by chemical bath deposition has direct energy gap

Fig7. represents the effect of different deposition temperature on the optical energy gap, the diagram shows that the energy gap decreases from 2.8 eV at temperature 40 °C to 2.6 eV at 50 °C the reason for the low energy gap is the increase in energy Kinetics of the molecule that lead to increased interaction between ions and thus the growth of granules and thus increase particle size Affecting the thickness of the film.

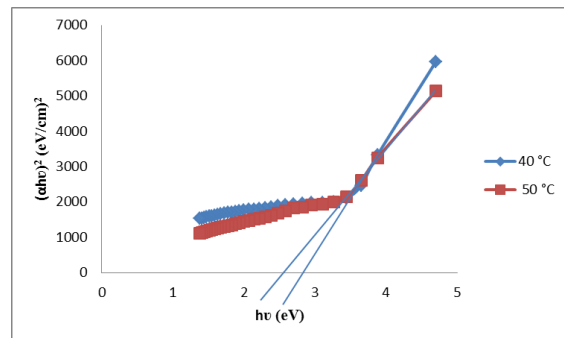


Fig7. Effect of deposition temperatures(40,50) °C in the optical energy gap

Conclusions

- 1- Thin Films Sb₂S₃ were polycrystalline in orthorhombic structure.
- 2- Sb₂S₃ thin film can be deposited at room temperature by chemical method.
- 3-The measurement of the scanning electron microscopy (SEM) showed that increasing deposition temperature significantly affects the shape and the size of the granules forming the surface of the thin film.
- 4- The Sb₂S₃ thin film has a high optical transmittance rate of up to 80%
- 5- Optical studies revealed that direct band gap is 2.8 eV at 40° C and 2.6 at 50°C

[2] Sze, S. M. (1981). Physics of Semiconductor Devices, 2nd Edition, John Wiley and Sons,.

- [3] Wasa, K. (2004). Thin film Materials Technology. William Andrew, Inc.
- [4] Solymar, L. and Walsh, D. (2004). Electrical Properties of Materials, Seven Edition, Oxford,.
- [5] Li, K; Huang, F. and Lin, X. (2008). Pristine narrow-bandgap Sb_2S_3 as a high-efficiency visible-light responsive photocatalyst. *Scripta Materialia*, **58**:834-837.
- [6] Krishnan, B. (2008). On the structure, morphology, and optical properties of chemical bath deposited Sb_2S_3 thin films. *Applied Surface Science*, **254**: 3200-3206.
- [7] Salem, A. and Selim, M. (2001). Structure and optical properties of chemically deposited Sb_2S_3 thin films. *Phys. journal of physics D:Applied physics*, **12**: 34.
- [8] Cao, X. (2006). Template-Free Preparation of Hollow Sb_2S_3 Microspheres as Supports for Ag Nanoparticles and Photocatalytic Properties of the Constructed Metal-Semiconductor Nanostructures. *Advance. Functional. Materials*, **16**: 896-902.
- [9] Messina, S; Nair, M. and Nair, P. (2007). Antimony sulfide thin films in chemically deposited thin film photovoltaic cells. *Thin Solid Films*, **515**:5777-5782.
- [10] Mathew, N. et al. (2011). Investigations on the Se doped Sb_2S_3 thin films. *Chalcogen. Letters*, **8**:441-446.
- [11] Rajpure, K.Y. and Bhosale, C.H. (2000). A study of substrate variation effects on the properties of n- Sb_2S_3 thin film/polyiodide/C photo electrochemical solar cells. *Materials. Chemical. Physics*, **64**:14-19.
- [12] Tigau, N. C. et al. (2005). The influence of the post-deposition treatment on some physical properties of Sb_2S_3 thin films. *Journal of Non-Crystalline Solids*, **351**:987-992.
- [13] Chopa, K. L. (1969). thin film phenomena. McGraw hill. New. York.
- [14] Mane, R.S. and Lokhande, C.D. (2003). Thickness-Dependent Properties of Chemically Deposited Sb_2S_3 Thin Films. *Materials Chemical and Physics*, **82(2)**: 347 – 354.
- [15] Osuwa, J. C. and Osuji, R. U. (2011). ANALYSIS OF ELECTRICAL AND MICRO-STRUCTURAL PROPERTIES OF ANNEALED ANTIMONY SULPHIDE (Sb_2S_3) THIN FILMS. *Chalcogenide Letters*. **8(9)**:571.
- [16] Desai, J. and Lokhande, C.D. (1995). Solution growth of microcrystalline Sb_2S_3 thin films from thioacetamide bath. *Journal of Non-Crystalline Solids*, **181**:70-76.
- [17] Chate, P. A. et al. (2015). Characteristics of Sb_2S_3 Thin Films Deposited by a Chemical Method. *International Journal of Thin Films Science and Technology*,(**3**): 237-242.
- [18] Lokhande, C. D. et al.(2002).XRD, SEM, AFM, HRTEM, EDAX and RBS studies of chemically deposited Sb_2S_3 and Sb_2Se_3 thin films. *Applied Surface Science*, **193**: 1-10.
- [19] Salem, A.M. and Selim, M.S (2001). Structure and optical properties of chemically deposited Sb_2S_3 thin films. *Journal of Physics D: Applied Physics*, **34**:(**1**).
- [20] Ezema F.I. et al. (2009). Optical and structural properties of amorphous antimony sulphide thin films effect of dip time. **5** : 145.
- [21] Ezema, F. A. et al.(2007). Optical Properties and Structural Characterizations of Sb_2S_3 Thin Films Deposited by Chemical Bath Deposition Technique. *Turkish Journal of Physics*, **31**: 205-210.
- [22] Chiang, Y.M. and Kingery, W.D. (2007). Compositional changes adjacent to grain boundaries during electrical degradation of ZO Nanoparticles. *Sensors*, **7(2)**: 185- 201.
- [23] Yao, N. and Wang, Z. L. (2005). Handbook of microscopy for nanotechnology. Kluwer Academic publishers , Boston.
- [24] شريف, احمد. خيرى شريف وجماعته.(2000). فيزياء الجوامد. مطبعة دار الفكر العربي .

تأثير درجة الحرارة على الخواص التركيبية والبصرية للأغشية الرقيقة Sb_2S_3 المحضرة بطريقة

الترسيب بالحمام الكيميائي

نيران فاضل عبدالجبار¹ ، رائد عبد الوهاب اسماعيل² ، مصطفى واثق فتحي¹

¹قسم الفيزياء ، كلية التربية للعلوم الصرفة ، جامعة تكريت ، تكريت ، العراق

²قسم الفيزياء ، كلية العلوم ، الجامعة التكنولوجية ، بغداد ، العراق

الملخص

في هذه الدراسة استخدمت طريقة الترسيب بالحمام الكيميائي للأغشية الرقيقة Sb_2S_3 المترسبة على الركائز الزجاجية. قمنا بتحليل الخصائص البصرية والتوصيف التركيبي للأغشية الرقيقة Sb_2S_3 . درست الخواص التركيبية للأغشية الرقيقة بواسطة حيود الأشعة السينية (XRD)، المجهر الإلكتروني الماسح (SEM)(EDAX). أظهر نمط XRD ان الأغشية الرقيقة كانت متعددة التبلور، وأظهرت EDAX ان مكونات العناصر هي ذات قيم مقاربة ومتوازنة كيميائياً (أي تحقق التوازن الكيميائي للطور Sb_2S_3). أظهرت الخصائص البصرية ان فجوة الطاقة البصرية عند $40^\circ C$ هي 8.2 eV وعند درجة الحرارة $50^\circ C$ هي 2.6 eV ، وان النفاذية البصرية عند $40^\circ C$ هي 80% وعند درجة حرارة $50^\circ C$ تبلغ حوالي 60%.