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ENHANCEMENT IN2S3NANOSTRUCTURES OPTICAL AND ELECTRICAL CHARACTERISTICS USING SPRAY PYROLYSIS GROWTH AS PROMISING MATERIAL FOR OPTOELECTRONIC APPLICATIONS

Neran F. Abd JABBAR[1], N.K.HASSAN [2] & Raid A.ISMAIL[3]

Abstract

In the present work, indium sulfide In2S3 thin films were grown on amorphous glass substrate by the chemical spray pyrolysis technique .The different molar ratio of In2S3 powder and thiocyanate (0.05,0.1,0.15) M used to grow In2S3 nanostructure with160nm thickness on the glass substrate under 310 Co temperature. Thickness of the films were measured by optical interferometer method. Structural properties were examined using X-Ra diffraction analysis is revealed that all the films were polycrystalline in nature with a dominant 0021peak which indicates that the In2S3 nanostructures are cubic phases. The evaluated crystallite size varied in the range 67.64-81.82nm with the increase of molarity. SEM analysis revealed that all The films have no voids and cracks. Optical properties of the grown films showed that the direct band gap values were found to decrease in the range 3.1-2.75eV which are means that it has the possibility of using indium sulfide in the manufacture of optoelectronic devices. Electrical properties using Hall effect measurement showed that all films N_type semiconductor. the conductivity for all films decreases with increasing of molarity. Results indicates the possibility of using indium sulfide in the manufacturing of detector or a gas sensor.

Keywords: Indium Sulfide, Chemical Spray Pyrolysis Technique, Band Gap Energy , Absorption Coefficient, Hall Effective , X-Ray, AFM.

[1] Tikrit University, Iraq, niran1964niran@gmail.com, https://orcid.org/0000-0002-0228-0857
[2] Tikrit University, Iraq, nadimkh4@tu.edu.iq
[3] Technology University, Iraq

1. Introduction

Among several materials, indium sulfide is an important material because of their importance in fundamental research and wide range of applications. In2S3 is a (III-VI) promising semiconductor materia for optoelectronic and photovoltaic applications due to its chemical stability[1,2] ,transparency and photo conducting behavior. Indium sulfide is an N type sem-iconductor presenting three forms a defect cubic β - structure under adjacent conditions, a defect spinel β - In2S3 formed at(693)K and β - In2S3 formed at 1013K [3,4]. Also, β - In2S3 is the constant phase of In2S3 from room temperature to 693 K. and it forms in a defect spinal lattice with a high degree of vacancies, ordering tetrahedral sites[5] .

Deposition of In2S3 thin films has been explored by distinct techniques such as(physical vapor deposition, chemical bath deposition (CBD), spin coating and spray pyrolysis) [6].The spray pyrolysis technique has been widely used to deposit binary ,thermal evaporation [7,8]and Electrodeposition(ED)[9].

Few papers of indium sulfide doping with element like aluminum, cobalt, sodium, etc. Are reports in the literature. So, N. Kamoun et, al observed an increase of oxygen adsorption in samples with indium sulfide doped with aluminum [10]

In the present the binary In2S3 thin films have been deposited on the glass substrate by(CSP) technique for different concentration molar (0.05, 0.1, 0.15) M because of its simplicity and low cost. In addition it allows to incorporation of different dopants. The structural, optical and electrical properties was studying. The participation in this article was motivated by its applications in optical, Electronic devices as buffer class in the photoelectric structures and a application in solar cells of nanotechnology [11].

2- Experimental

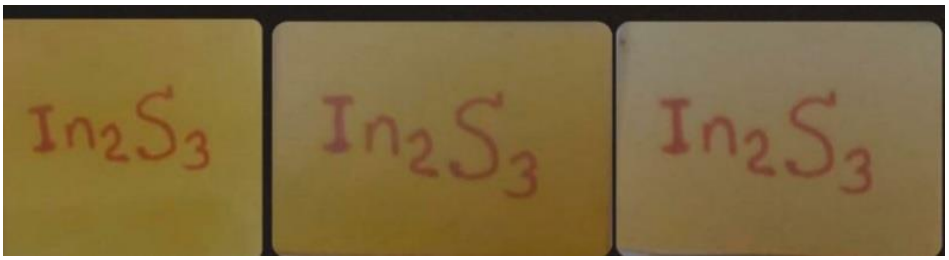
2-1 Materials and Films Preparation

The thin films In2S3 was prepared by CSP method with a temperature of 310Co by preparing the dimensional glass deposition bases(2.5*2.5)cm .The indium sulfide solution was prepared through two materials indium chlorate InCl3 produced from the company (secilz -hannower Riedal -dehaeAG) with a purity of (99.8 %) and solution of thiostamide(CS(NH2)2 prepared from the company (PDH) and the preparation of films with molarity as shown in Table (1) . The substrate temperature was kept at 310 Co for all samples.

Table (1) weight of materials used to obtain the required proportions of indium sulfide

In2S3 M	InCl3(g)	CS(NH2)2 (g)	Water(ml)
0.05	0.55	0.177	50
0.1	1.119	0.355	50
0.15	1.658	0.532	50

The glass bases are left on the heater for a period of 15 to 20 min, before starting to spray to ensure that the surface of the bases reaches a temperature310 Co.



0.15M 0.1M 0.05M

2-2 Mechanism of spray pyrolysis.

The glass bases are placed on the thermal heater in the middle approximately so that it is suitable in terms of the thermal distribution of the heater and the distance between the nozzle of the device and the

surface of the base is 29 cm to make sure that the solution arrives and is perpendicular to all parts of the glass base and the amount of falling solution is controlled through the solution descending valve .The volume spray was 10 mL, the spray 3mL\min, the air compressed pressure 3 bar.

2- 3 Characterization technique

The structural and chemical phases of the In2S3 films were calculated by X-ray diffract meter model (ADX 2700) current (30mA) voltage (40 kv) source of X-ray (Cu Kα ,λ=1.541A0) .Grain size of the films was calculated from the XRD pattern using Debye Scherer's formula (D= $k\lambda \backslash \beta cos\theta$),where D is the grain size, β is the full width half maximum of the peak .

The optical properties using optical absorptionspectrum we observed using (UV-vis –NIR doble beam spectrometer) over the wavelength rang300-1100nm.

The electrical conductivity of theas- deposited films was found by Hall Effect measurement system by(HMS -3000)model. A Hall coefficient (RH) is determined by measuring the Hall voltage(VH) that generates the Hall filed (EH) across the sample of thickness (t) by equation (1) :[12,]

RH=VH\I *t\B----------(1)

From the values of Hall coefficient, the type of semiconductor carries can be found, if RH is negative or positive for n-type and p-type, respectively.

If the conduction is due to one type e.g. electrons. can measure the mobility as

$\mu H = \sigma[R_{}$]----------(2)

3-Results and Discussion

The X-ray diffraction pattern of In2S3 films of different precursor concentrations deposited at substrate temperature of 310Co is shown in Fig.1.The XRD measurement exposed that all the films were polycrystalline with three pattern(109),(0012),(1015) , with mixed phase of both cubic and tetragonal structure with different precursor concentrations, and the direction prevailing at top0012 at angle 33.46o. .which were matched with standard peaks .The intensity of the diffraction peaks with cubic phase turned more intense and sharp with increase of precursor concentration ,which notice an improvement to the crystallinity of the grain layers. This result agrees well with [14,15,16,17].

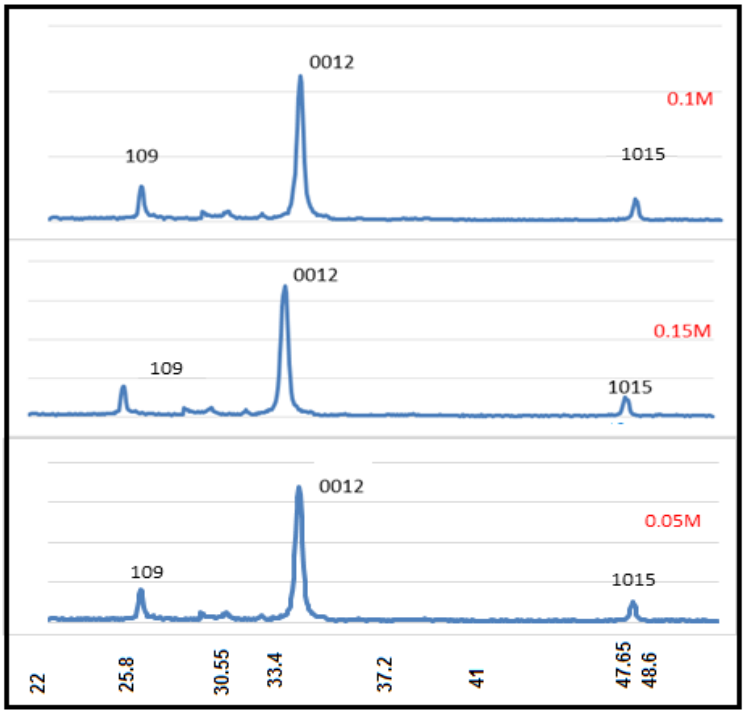


Fig 1:X-Ray pattern of In 2S3 thin films with different molarity

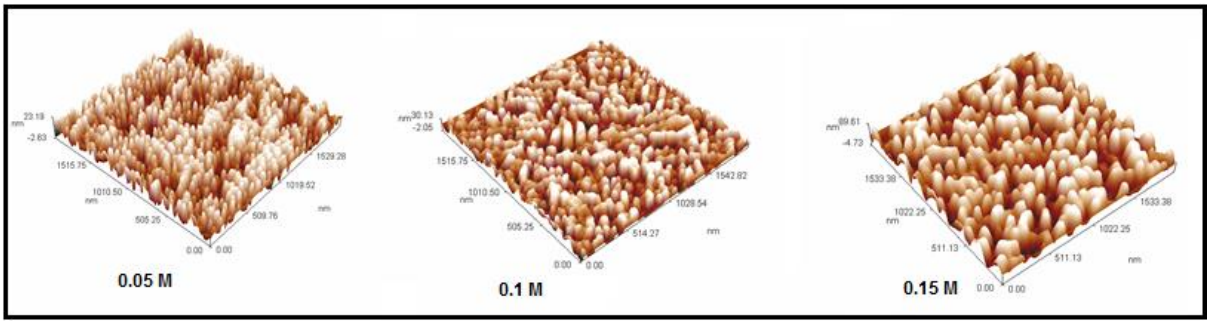


Fig 2: 3D AFM image of In2S3 thin films

Figure (2) shows the images of the analytical atomic force microscope (AFM) represent the prepared films . The grains have granular sizes ranging from (67.64,68.50,81.8)nm from concentration of (0.05,0.1,0.15)M respectively .We find that the granular size increase with increase in the molar concentration of the precursors, which is due to the increase in the thickness of the film..

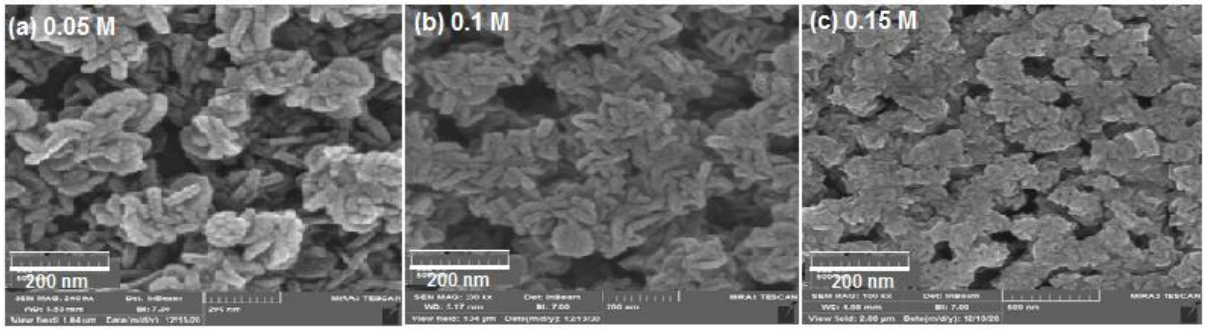


Figure 3: SEM image of In2S3 thin films

Figure (3) shows the SEM images of the different grain shapes provide microscopic information about the surface topography .We note that the films cover the surface of the subtrates and there are no holes in them. By increasing the concentration ,the surface contains larger grains ,as a result of increasing the crystalline.

Fig(4) shows the optical transmittance spectra of the as deposited In2S3 films of different molarity concentrations. It can be ascertained that the transmittance of the as-deposited of precursor concentration(0.05)M (70 -80$^{\%)}$ While the precurrsor concentration at (0.15) that decreased from60% to 50$^{\%}$ which may be due to the increase in the thickness of the film ,and the absorbency of the films and those lead to decrease in the films, Conversely, in fig (6) the absorbance spectrum will be reduced

The Energy band gap of the deposited thi films measure using the relation [αhv=A(hv-Eg)1\2] were A is the energy independent constant, which(1\2) is for a direct allowed transition. The Optical absorption spectra of In2S3 films was recoded at room temperature by taking glass as reference in order to avoid effect of substrate on absorbance .As shown in fig.(5) The variation of ($ahv)\ and\ (hv)for$ In2S3 films is a straight line indicating the transition involved is of direct one[14] band gap energy is determined by extrapolating the straight line portion to the energy basis at $(\alpha$ =0) and is found to be2.75 and 3.1 ev Shown in Table NO.(2) . with increase in the different molar from0,05M to 0.15 M ,Shown in Fig (5) a and b. this is consistent with the literature[18,19]. The sharp reduction of energy band gap at higher precursor concentration could be owing to th constitution of localized states in the band gap. In this study the improvement in the particle size and the stoichiometric deviations could contribute to the decrease of generally energy band gap of the films with the increase in the precursor concentration. This result agrees well that presented in reference[14,20] .

Table (2)The energy gap values for the In2S3 thin films with different concentration

Molarity concentration (M)	0.05	0.1	0.15
Energy gap (ev)	3.1	2.9	2.75

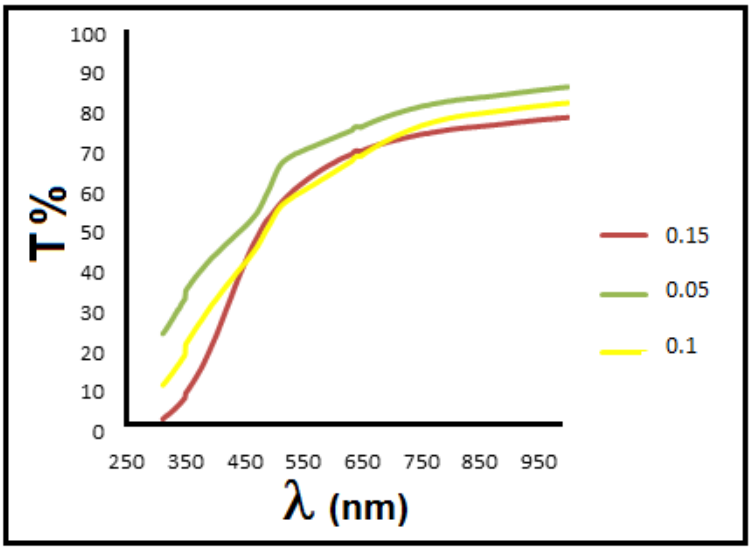
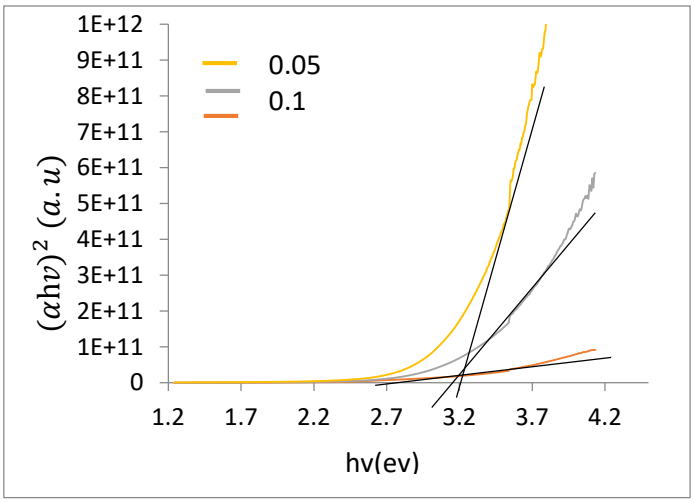
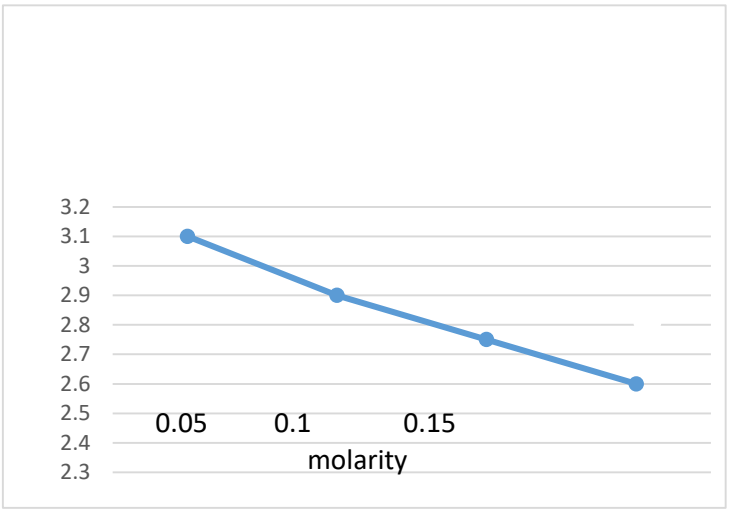


Fig 4 :. Transmittance versus Wavelength graph of In2S3 thin films





(a) (b)

Fig.5.(a),($(\alpha hv)^2$) versus (hv) of In2S3 thin films with different molarity ,(b)the photon energy as a function of the molarity.

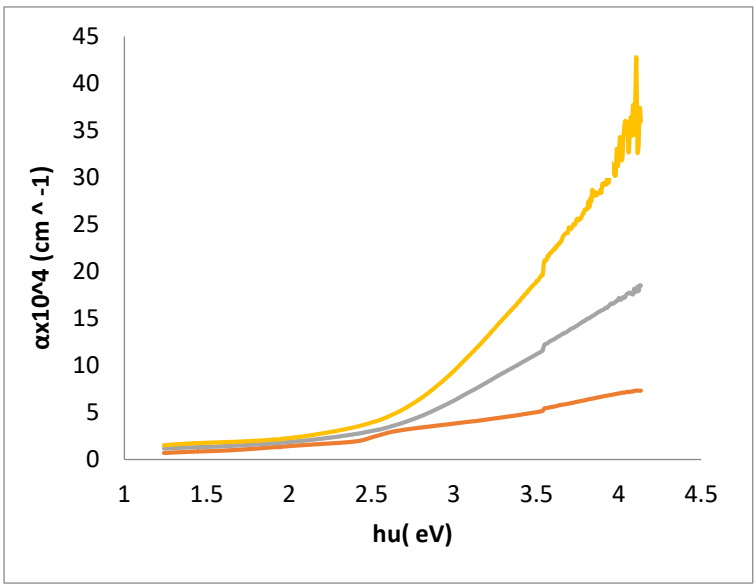


Fig.6. The absorption coefficient of the In2S3thin films.

The Electrical properties

Resistivity, conductivity, mobility of In2S3 thin films deposited at different molar ratios were determined by Hall Effect measuring ,the measured values are listed in the Table(3).The Hall coefficient values supports that the films had an N-type characteristic fig (7) shows the variation in the resistivity ,mobility and conductivity of the films as a function of precursor concentration .The resistivity of the as deposited films decreases with increasing in molarity from0.05M to 0.15M. The n-_type conductivity in I In2S3 is owing to sulphur vacancy and interstitial indium atoms. both catting as donors. The emphasis in conductivity with increase with increasing molarity may also be due to the large density of extrinsic traps at the grain boundaries .This agrees with the source[20].The mobility increases as a result of build up again and the crystallinity growth of the material. This is closer to what he found Timoumi and S.Alaya [21].

Table 3: Electrical properties of In2S3thin films at different molarity

Molarity M	Mobility (cm2\vs)	Resistivity Ώ cm	conductivity 1\ Ώ cm
0.05	3.190E+2	8.555E+4	1.150E-5
0.1	3.233E+2	8.551E+4	1.170E-5
0.15	3.499E+2	1.357E+4	7.365E-5

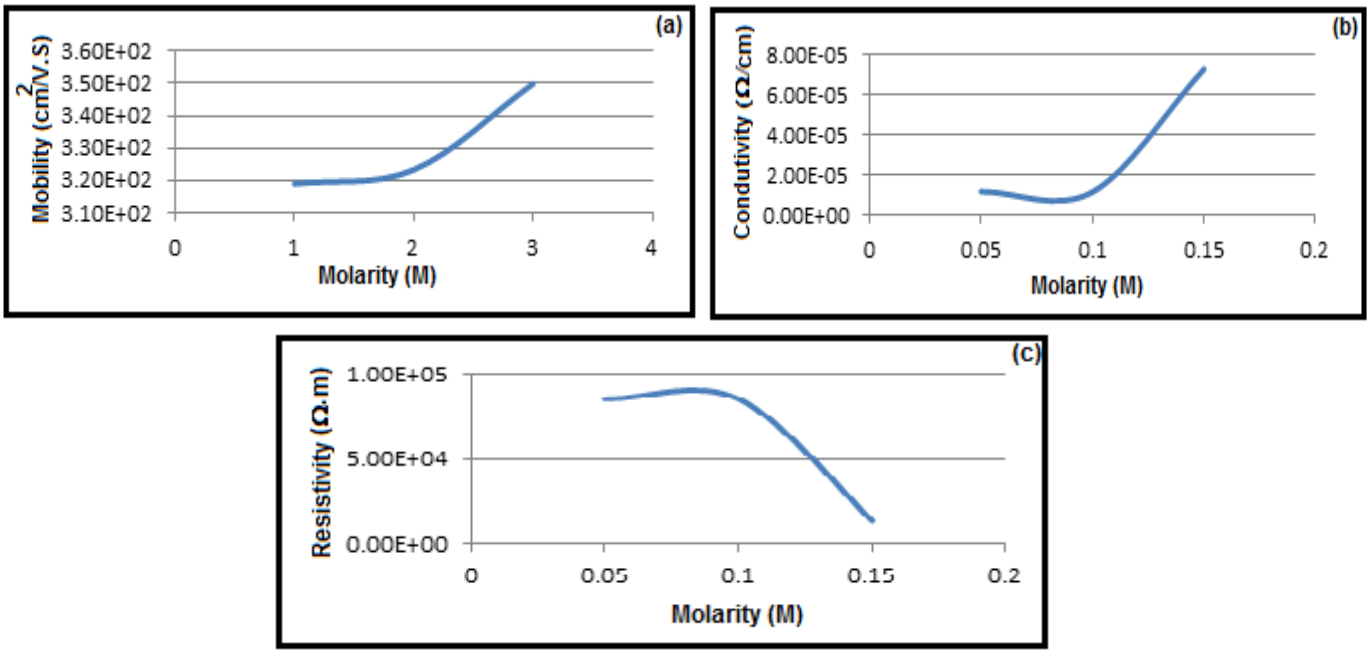


Fig.7. Electrical properties (a- mobility, b-conductivity, c-resistivity) of In2S3 thin films at different molarity

Conclusions

The thin films have been prepared by chemical spray pyrolysis method at different molarity (0.05 ,0.1,0.15) M. the thickness of the films162 nm. The films have a cubic crystal structure with a orientation 0012. In2S3 films exhibit transparency over(70-80)% at 0.05M in the visible and infrared region. The band gap is 2.275 to 3.1eV for direct transitions. The Hall effect measurement confirmed that the In2S 3 films have negative Hall coefficient indicating the film are N-type . The electrical resistivity of the as-deposited In2S 3 thin films is decreased by increasing molarity. a The In2S 3 films prepared are a promising candidate for photovoltaic and optoelectronic devices.

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