Electrical and structural properties of ZnS thin film

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Abstract

Semiconducting Zinc sulphide (ZnS) thin filmwas deposited on glass substrate usingchemical spray pyrolysis technique.The suitable deposition temperature was 400 ±3°C, and the thickness of the films was found to be 420 ±5nm. The X-ray diffraction (XRD) analysis showed that the film was polycrystalline with grain size of crystallite 16 nm. The electrical properties were studied for prepared film, and the results showed a linear behaviour of I-V characteristics at the voltage range of 30 -100 V. Resistivity of ZnS sample decreases with temperature, and found to be $9.91 \times 10^{2} \Omega\, cm$ at room temperature while the conductivity was $1.01 \times 10^{-3} \Omega^{-1}\, cm^{-1}$. The activation energies were found to be temperature dependent and showed two values 0.21(eV) for temperature range (293-453)K and 0.233(eV) for temperature range (463-513)K. Hall coefficient (R_H) was calculated, its value pointed that the films was n-type, and the carrier concentration was estimated as $4.21 \times 10^{13} \Omega\ (\frac{1}{cm^3})$, while the mobility was $149(\frac{cm^2}{V.s})$.

Key words: Zinc sulphide **(**ZnS), thin film, electrical properties, structural properties.

Introduction

Zinc sulfide (ZnS) is one of the first semiconductors discovered and be also an important semiconductor material, which has attracted much attention from the viewpoint of fabrication of many optoelectronics devices because of their unique properties such as quantum size effect and abnormal luminescence phenomenon [20]. ZnS nanoparticles, several potential and actual applications were reported, i.e. in optoelectronic devices, light emitting displays, photocatalysis, solar cells and luminescent materials, and many of these applications require nanostructures with the high dispersion, stability and size uniformity [2, 17, 19]. It has a high absorption coefficient in the visible range of the optical spectrum and reasonably good electrical properties in which the direct wide band gaps for cubic and hexagonal phases were 3.72 and 3.77 eV, respectively[4]. Besides, ZnS can be used as a light emitting diode in the blue to ultraviolet spectral region[1], and also as a reflector, because of its high refractive index value. However, deposition of a high quality ZnS thin film over a large area is required for electroluminescent devices and solar cells. [4,12] Many growth techniques have been reported to prepare ZnS thin films, such as sputtering, pulsed-laser deposition, and metal organic chemical vapor deposition, electron beam evaporation, photochemical deposition, thermal evaporation, chemical spray pyrolysis, sol-gel processing, co-precipitation and chemical bath deposition[1, 10, 12,15]. There have been various studies on the bulk and thin film characteristics of ZnS by different methods, but in the present work, the chemical spray pyrolysis was used to prepare ZnS thin film and study its characterization for structural and electrical properties using XRD analysis, resistivity, electrical conductivity, activation energy and Hall measurements such as carrier concentration and its mobility.

Theoretical consideration

The theoretical ideas of structural properties comes from X-ray diffraction analysis (XRD) in which their diffractogram peaks are performed as a result of instructive interference of diffracted wave front. The geometric explanation of this diffraction could be represented by the formulation of Bragg's law:[21]

$$n\lambda = 2d_{hkl}\sin\theta \ldots\ldots\ldots\ldots (2.1)$$

where λ is the wavelength of radiation , d_{hkl} is the spacing between (hkl) planes, and θ is the diffraction angle. The crystallite size has been estimated, from the full width at a half of maximum intensity of the strongest diffracted peak (FWHM), by the Schrrer relation[13]:

$$l = \frac{0.94\lambda}{\beta cos\theta} \ldots\ldots\ldots\ldots\ldots (2.2)$$

where, l is the crystallite size, and β is the angular width (FWHM).

The theoretical relations of electrical properties used in our workreturns to Ohms theory. The resistivity is calculated using the following equation:[21]

$$\rho = \frac{RWt}{L} \ldots\ldots\ldots\ldots\ldots (2.3)$$

where ρ is the resistivity, t is the thickness, L and W are the length and the width of the sample respectively. If $W = L = length\ of\ electrode$, the Eq. (2.3) becomes

$$R = \frac{\rho}{t} = R_s \ldots\ldots\ldots\ldots\ldots (2.4)$$

The above relation reveals that resistance R_s of square film does not depend on the size of square, it depends only on resistivity and thickness of the film, where R_s is known as sheet resistance of the film and is expressed in Ohms per square (Ohms/□). It is very useful parameter for the evaluation of thin films for optoelectronic applications.[6 , 9]

The electrical conductivity σ was investigated by the relation:

$$\sigma = \frac{1}{\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

The electrical conductivity can be related with mobility by the relation;

$$\sigma = ne\mu \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.6)$$

Where n is the carrier concentration, e is the electron charge ($e = 1.6x10^{-19}$C) and μ is the mobility .The activation energy was obtained using the relation:[14]

$$\sigma = \sigma_0 \exp\left(-\frac{E_{ac}}{KT}\right) \ldots\ldots\ldots\ldots (2.7)$$

where, σ_0 is a constant, E_{ac} the activation energy for conduction, K the Boltzman constant and T the absolute temperature. E_{ac} can be calculated from slope of the curve (lnσ versus $\frac{1}{T}$) .

The equations of Hall effect which can be used in this work are:

$$V_H = \frac{B_Z R_H}{t} I_x \ldots\ldots\ldots\ldots\ldots (2.8)$$

Where V_H is the Hall voltage in the Y- direction, R_H is the Hall coefficient, B_Z is the magnetic field in Z-direction, t is the thickness of the film and I_x is the current in the X-direction. R_H can be calculated by slope of the relation (2.8), while the carrier concentration n can be calculated from Hall effect by the following relation:

$$R_H = \frac{1}{ne} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.9)$$

The carrier mobility can be obtained from Hall effect by substituting (2.9) in (2.6).

$$\sigma = \frac{\mu}{R_H} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.10)$$

Experimental work

Zinc sulfide thin film was deposited on glass substrates (2.5 x 7.6 cm^2) using spray pyrolysis technique, this technique is widely used for the large-scale production of films owing to its low production cost and simplicity of operation. The glass substrate was cleaned by distilled water and then by pure alcohol for 10 minutes. It was further cleaned in ultrasonic bath using distilled water for 20 minutes and dried by hot flowing air using blower. Solution containing Zinc Chloride ($ZnCl_2$) and Thiourea ($SC(NH_2)_2$).of molar concentration 0.1 M/L were used to prepare

ZnS thin film. The prepared solution was sprayed at a spray rate of 5 ml/min onto clean glass substrates maintained at different temperatures 300^{o}C, 350^{o}C, 400^{o}C^{o,} and 450^{o}C, and the films have been checked for homogeneity and measuring thicknesses, by multiple beam interferometer method, using He – Ne laser with monochromatic wavelength 632 nm, therefore, the thickness measurements of these films could not be obtained if the film is not homogeneous, while the homogeneous film can be easily measured. So, the thickness of the film deposited at 400 C^o was found to be the most homogeneous film than theother films deposited at 300^{o}C, 350^{o}C and 450^{o}C temp., and its thickness was found to be (420±5) nm. This is in agreement with other previous studies which have showed that films deposited at 400^{o}C has homogeneity[22].The homogenous film was cut into small square samples with dimensions of 10x10 mm^2 , and covered with clean clothes inside clean box to avoid contamination on the film surface before aluminium (Al) electrodes deposition, previous studies have shown the same sample preparing method[9]. Suitable masks were made from aluminum foil for depositing electrodes, where pure aluminium thin film electrodes were deposited on the square film by thermal evaporation technique with vacuum 10^{-6} Torr and temperature 700^{o}C to obtain Ohmic contact with two prope, according to equation (2.3), in which the length of both electrodes was the same, and equal the dimensions of square sample.

The structures of the prepared thin films were obtained using the XRD techniques, using radiation from CuKα radiation target (λ=1.54 A^o) in the range of 2θ between 20^o–60^o. The peaks of x-ray diffractogram were performed as a result of instructive interference of diffracted wave front from parall plane of crystal. The inter planer distance $d_{(hkl)}$ for different planes was measured by using equation(2.1). The grain size of crystallite can be calculated, using the equation (2.2).

The electrical properties studied in this work, such as I-V characteristics resistance, activation energy and Hall measurements were measured, using the sensitive digital electrometer (Kiethley model 610 B) in which DC Resistivity and activation energy of the film can be calculated by the equations (2.4) and (2.7), respectively and carrier concentration and its mobility can be calculated by equations (2.9) and (2.10) respectively.

Results and Discussion

Figure (4.1) shows the x-ray diffraction of ZnS filmIn which the broad peaks were observed at 2θ values of 28.8°, 33.5°, 48.2° and 57.8°. This schematic showspolycrystalline with cubic structure in nature with (111) plane in preferred mode, which closely matches with the (111), (200), (220) and (311) crystalline planes of the cubic structure of ZnS reported in the ASTM cards data , and is in agreements with previous studies also[18]. Since the card does not show any new XRD peaks differences with ASTM cards peaks of ZnS film, that mean the sample is pure. The grain size of the crystallites is approximately 16 nm, which is different than the values obtained from other studies [3,22] because of the different preparation methods and purity.

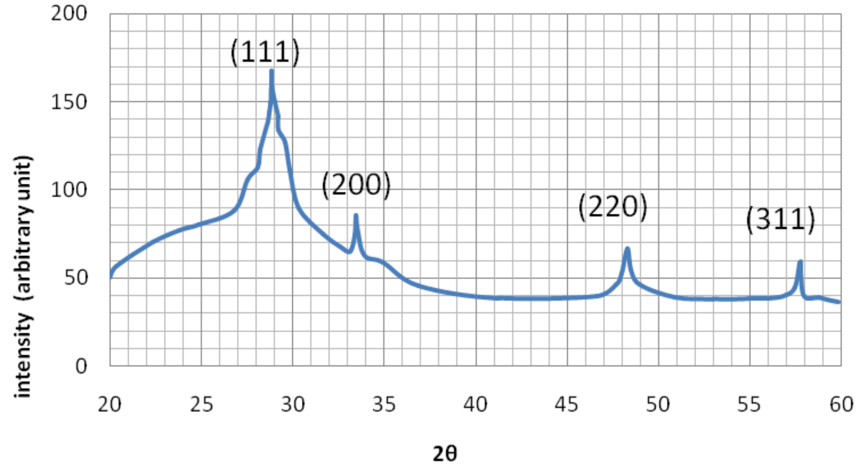

fig.(4.1) x-ray diffriction of ZnS film

Figure (4.2) shows the linear I-V characteristic behaviour for ZnS in which the result indicates that the prepared films show ohmic behaviour. This result is in good agreement with the result of - Huang Jian et al.[5] Besides, the linearity may be due to the decrease of carrierstrapping processes, as a result of the increase in the applied voltage .

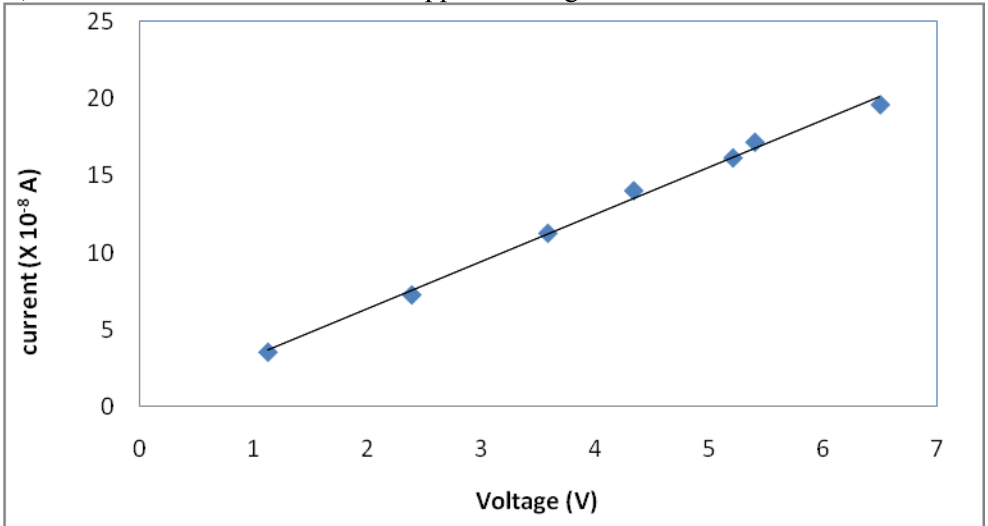

fig. (4.2) *I– V* characteristics of ZnS film

The electrical resistance of the film can be obtained by determining the reciprocal slope of the linear I-V curve (Fig. 4.2), and was found to be equal 32.6 MΩ and, therefore, the ZnS film is of high resistance which depends on the sample dimensions. The DC resistivity has been investigated by using equation (2.4) which is be found equal to $9.91 \times 10^{2}\,\Omega cm$ atroom temperature. Also conductivity has been calculated by equation (2.5), and found to be $1.01 \times 10^{-3}\,\Omega^{-1} cm^{-1}$. Such results of resistivity and conductivity of ZnSfilm belong to semiconductors range[7,8].

Fig.(4.3) shows resistivity of ZnS sample decrease with increasing temperature, which indicates the semiconducting nature of thin film[21]. Also, the conductivity studies on film shows that the film exhibits two activation energies: (0.21 eV) at temperature region (293K-435K) and (0.233eV) at region (463-513) as shown in Figure (4.4). Such result is in agreement with other results.[11], and indicate that the conductivity increases with increasing temperature.The results may be due to the presence of two donor levels- one deep and the other shallow near the bottom of the conduction band from which the thermal activated carriers is translated to conduction band to increase the conductivity.

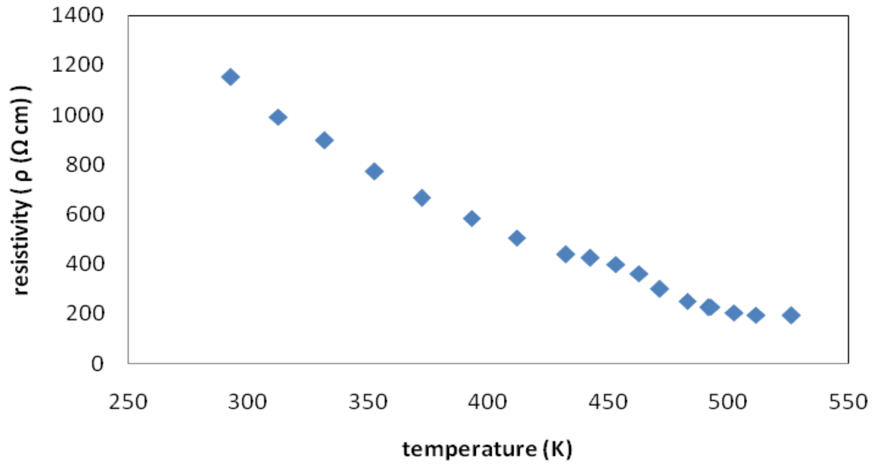

fig.(4.3) resistivity (ρ) vs. temperature

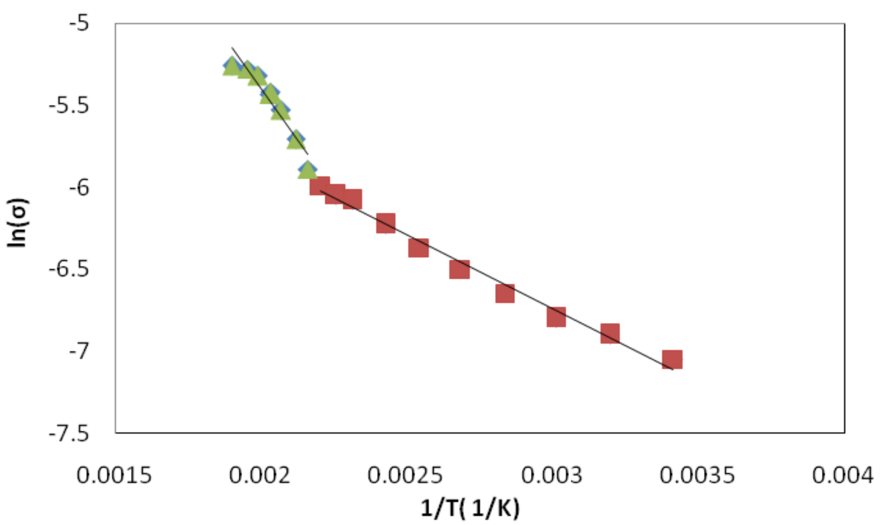

fig.(4.4) ln (σ) vs. reciprocal temperature (1/T) for ZnS film

The Hall results for ZnS thin films, such as Carrier concentration, type of carriers and hall mobility; have been determined from Hall measurements for ZnS thin film.

Fig.(4.5) shows the plot of Hall voltage versus the current for ZnS thin films, then the Hall coefficient (R_H) has been calculated from constant proportionality of equation (2.8) (slope of the line curve). The R_H value has obtained $1.49 \times 10^{-1} \frac{m^3}{C}$ and it indicates that the film was n-type semiconductor, the carrier concentration was estimated as $4.21 \times 10^{13} \left(\frac{1}{cm^3}\right)$ and the Hall mobility was $149 \left(\frac{cm^2}{V.S}\right)$. Such results are in agreement with the results of previous studies. [7,,8,16]

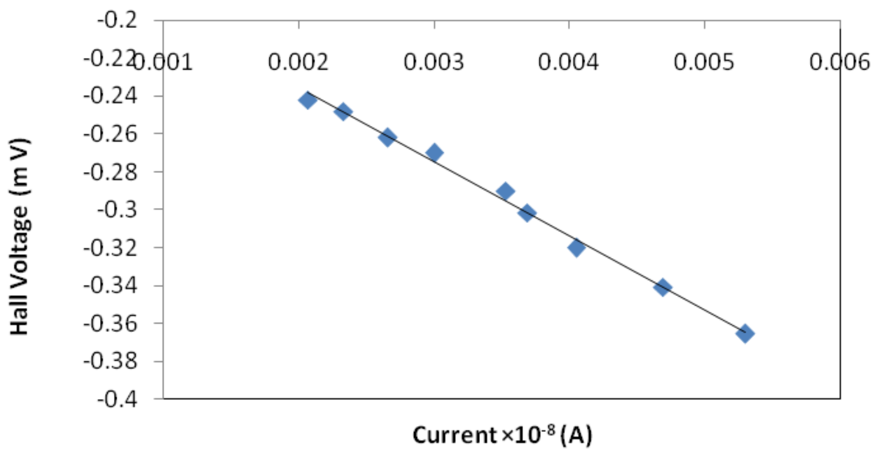

fig.(4.5) Hall voltage as a function of the current for ZnS thin film

Conclusion

1-The deposition temperature (400°C) is a suitable degree to prepare homogenous ZnS thin film better than other deposition temperatures: 300C°, 350C°, and 450C°for thickness (420 nm).

2- The electrical measurements at room temperature showed that the film represent as n-type semiconductor with carrier density ($4.21 \times 10^{13} \left(\frac{1}{cm^3}\right)$), resistivity ($9.91 \times 10^2 \Omega cm$) and mobility $149 \left(\frac{cm^2}{V.S}\right)$.

3- The structural measurements showed that the film structure was polycrystalline with grain size 16nm.

4-The above obtained characteristics make the ZnS film as a good material for semiconducting devices.

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الخواص التركيبية والكهربائية لغشاء كبريتيد الزنك (ZnS) الرقيق

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الملخص

رُسب الغشاء الرقيق لمادة كبريتيد الزنك (ZnS) باستخدام تقنية الرش الكيميائي الحراري على شريحة زجاجية عند درجة حرارة ترسيب مناسبة (400±3ºC) بسمك (420±5nm). حُلل الغشاء باستخدام حيود الأشعة السينية (XRD) وأظهرت النتائج أنَّ الغشاء يمتلك بنية متعددة البلورات, حجم الحبيبة البلورية فيه 16 nm تقريباً.. دُرست الخصائص الكهربية للغشاء الرقيق وبينت النتائج وجود سلوك خطي لمنحنى تيار- جهد في المدى (V 100- 30) وتناقص المقاومة النوعية بزيادة درجة الحرارة، وقد بلغت قيمتها $9.91 \text{ x } 10^{2} \Omega\ cm$ عند درجة حرارة الغرفة، في حين كانت التوصيلية الكهربائية $1.01 \text{ x } 10^{-3} \Omega^{-1}\ cm^{-1}$. أظهرت النتائج أيضاً اعتماد طاقة التنشيط على درجة الحرارة والتي فيها تم الحصول على قيمتين 0.21eV و 0.233eV عند مديين من درجات الحرارة (293-453)K و (463-513)K على التوالي . حُسب معامل هول (R_H) وتبين إن الغشاء هو شبه موصل من نوع n ، وكان تركيز الحاملات يساوي $4.21 \text{ x } 10^{13} \Omega\ (\frac{1}{cm^3})$ في حين بلغت التحركية $149 (\frac{cm^2}{V.s})$.

الكلمات المفتاحية: كبريتيد الزنك ZnS، غشاء رقيق، الخواص الكهربية، الخواص التركيبية.