تأثير المعالجة الحرارية على الخصائص التركيبية والكهربائية لأشعة ZnS الرقيقة

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الخلاصة:
تناولت الدراسة تأثير التلدين على الخصائص التركيبية والكهربائية لأشعة ZnS الرقيقة المحضرة بطريقة التحلل الكيميائي الحراري، وتم تحليل النتائج باستخدام حيود الأشعة السينية ودراسة تأثير هول، أظهرت النتائج فحوصات الأشعة السينية بأن الأغشية المحضرة هي من النوع متعدد التبلور وذلك طور سداسي، وأن هناك زيادة في درجة التبلور بعد المعالجة الحرارية حيث ازداد حجم الحبيبات البلورية وكانت س(Dislocation density) عند القيم (18-40)nm وانخفضت قيم كثافة الانحراف ضمن الحدود (10^{12}-1.6\times 10^{12}) lines/cm، ولوحظ تغير المقاومة الكهربائية مع الحرارة، إذ انخفضت المقاومة بمقدار ثلاث مرات عن قيمتها قبل التلدين، بالإضافة إلى تغير قيمة طاقة التنشيط بقيم تتراوح بين (1.5-11) eV مع المعالجة الحرارية. ومن نتائج هول اتضح بأن الأغشية المحضرة هي من النوع السالب وذات تحريك بالحدود (10\pm 60) cm²/v.s. وهذه النتائج تؤكد حدوث تحسن في التركيب البلوري للأغشية بعد المعالجة الحرارية عند درجات (400-500)°C نتيجة لتقليص العيوب البلورية.
Influence of Heat Treatment on the Structural and Electrical Properties of ZnS Thin Films

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Abstract:

Zinc Sulfide thin films have been deposited onto glass substrates by spray pyrolysis method, the films were analyzed by X-ray diffraction and Hall Effect measurements. XRD analysis of the deposited and annealed films showed that all the films have polycrystalline with hexagonal structure. The effect of heat treatment enhances the grain size and improves the crystalline of the films, the grain size is found to increased from (18-40)nm, also the dislocation density (δ) decreased and in the range (1.6×10^{12} - 1.01×10^{12})lines/cm. Electrical resistivity is changed after the films were exposed to heat treatment, the value of resistivity was decreased about (3) times than that before annealing. Moreover the activation energy was decreased (1.5-1.1)eV by heat treatment. Hall measurements proved that ZnS thin film is an n-type semiconductor with electron mobility around 160±10cm^{2}/v.s. These results confirmed the improvement in crystallinity of the films with heat treatment at (400,500) °C because of decreasing crystal defects.

Key wards: ZnS thin films, structure, electrical properties, spray pyrolysis.

Introduction:

The II-VI group semiconductors are of great importance and this due to their applications in various applications among these, Zinc Sulfide thin film, is the most suitable for its utility in opto-electronic devices. ZnS has many advantages such as, high deposition rate, transparency at R.T
due to the broad band gap ($\approx 3.7$eV) and less sensitive about oxidation than ZnO[1], there has been a great interest in the study of charge carrier transport of ZnS which has become one of the most applied insulator in thin film electroluminescence devices[2]. ZnS is suitable for use in blue light emitting diodes, it has high refractive index about (2.35) [3]. polycrystalline and nanocrystalline ZnS have received much attention lately because of its probable important role in photovoltaic technology, optical coating, n-window layers for thin film heterojunction solar cell[4]. ZnS has a low exaction Bohr radius (2.5nm) that makes it nanoparticles interesting as small biomolecular probes for florescence and laser scanning microscopy [5]. several techniques have been used to produce ZnS thin films such, sputtering[6], chemical Bath [7] vacuum evaporation technique [8] spray pyrolysis method[9]. In this work, we report how thin films of ZnS were deposited on glass substrate using spray pyrolysis method, this method has been classified as one of the best cost effective techniques of thin films deposition. It is simple, cheap and easily reproducible and through it large area of thin films can be deposited without using sophisticated equipment. Structural and electrical properties have been studied of ZnS thin film as function of annealing temperature.

**Experimental:**

ZnS thin films were prepared by spray pyrolysis method using aqueous solution of zinc chloride and thiourea at molar ratio of 1:1, continuous film is formed on the hot substrate (350°C) by thermal decomposition of the material, the films deposited below 350°C are amorphous. Thickness of the film was measured by weight method and was 3000Å. Spray rate employed was 3ml/min, the obtained films were white to yellow, uniform and with good adherence to the substrate. The films were characterized by XRD and Hall Effect measurements, included the effect of heat treatment on the structure of the examined films. Thermal annealing of the films were done at different temperatures (400, 450, 500, 550°C) for 3hours by using an oven kind (L-C-Manfredi) in air atmosphere, then the films were allowed to cool. Electrical properties
of the films were carried out by monitoring the variation of electrical resistance (R) as function of temperature in the range (27 to 177)°C. Mobility and carrier concentration were determined by four-point probe in van der pauw configuration using uniform magnetic field of about 0.215T. The experimental errors were estimated to be in the order of 2.5% compared with the previous letters [10, 11].

**Results and Discussion:**

**Structural Properties:** XRD patterns of the as-deposited and annealed ZnS thin films are shown in Fig. (1), it can be seen that the films have polycrystalline hexagonal structure with strong (008) plane, and three subsidiary peaks of relatively low density corresponding to the (104), (105) and (106) planes are also observed, it can be estimated that the position of diffraction peaks is shifted toward higher 2θ compared with that of the as-deposited film, this peak shifting may be attributed to the residual stress stemming from different expansion coefficient of the film and the substrate [12]. During heating process, several mechanisms undergo in the films 1) recrystallization of ZnS films, 2) replacement of S with O by thermal diffusion, and 3) densification. It can be seen from Fig.(1) that at annealing temperature (400,500)°C, the grain growth results in smoothing the surface and consequently a reduction in surface defect states, hence high intense peak, but at t=(450,550)°C there is a decrease in the peaks intensity, broadening of the peaks and decrease in the grain size this result can be attributed to the film nature (porosity, texture) also XRD measurements indicate that ZnS film may be transform to mixed ZnS and ZnO at these temperatures (the heat treatment did not terminate the Zn-S bonds completely) these results were inconsistent with previous works [13,14]. The C-axis lattice parameters were obtained from the d-interplanner spacing of different peaks and XRD patterns using the equation[15]:

$$d_{hkl} = \frac{a}{(h^2 + k^2 + (a/c)^2l^2)^{1/2}} \text{------------------------(1)}$$

Where (hkl) are the reflection planes, the value of (c) for all the peaks was 24.92Å after annealing process and the values of (a) decreased
slightly from (3.880 to 3.707) Å, a decrease in lattice constant of the film is expected due to the increase in the diffraction angle. The dislocation density ($\delta$) was determined using the relation [16]:

$$\delta = \frac{15\beta}{4aD}$$

Where $\beta$ is the full width at half maximum and D is the grain size which was measured by using Dbye Scherer's formula [17]:

$$D = \frac{0.94\lambda}{\beta \cos \theta}$$

Where $\lambda = 1.54$ Å is the wavelength of x-ray. The calculated parameter ($a$), grain size ($D$) and dislocation density ($\delta$) after heat treatment are listed in table (1)

Table (1): XRD data for the as-deposited and annealed films:

<table>
<thead>
<tr>
<th>As-deposited ZnS thin film</th>
<th>Annealed film at 400°C</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$</td>
<td>$a(Å)$</td>
<td>$D$(nm)</td>
</tr>
<tr>
<td>29.4356</td>
<td>3.802</td>
<td>18</td>
</tr>
<tr>
<td>47.7869</td>
<td>3.813</td>
<td>25</td>
</tr>
<tr>
<td>57.7654</td>
<td>3.815</td>
<td>23</td>
</tr>
<tr>
<td>Annealed film at 450°C</td>
<td>Annealed film at 500°C</td>
<td>hkl</td>
</tr>
<tr>
<td>$\theta$</td>
<td>$a(Å)$</td>
<td>$D$(nm)</td>
</tr>
<tr>
<td>29.9798</td>
<td>3.725</td>
<td>22</td>
</tr>
<tr>
<td>48.9987</td>
<td>3.709</td>
<td>35</td>
</tr>
<tr>
<td>57.9879</td>
<td>3.707</td>
<td>25</td>
</tr>
</tbody>
</table>

It was observed that the dislocation density are lowered, the grain size are increased with the heat treatment at $t=(400,500)$ °C, this may be due to improvement in crystallinity and the quality of the films.

**Electrical Properties:** The resistivity was determined from the relation:

$$R = \rho l / A$$

where $l$ is the distance between two electrodes ,and $A$ is the product of length of the electrode and thickness of the film. The temperature dependence of the resistivity $\rho$ is given by:

$$\rho = \rho_0 e^{E_a/kT}$$

where $\rho_0$ is the pre-exponential factor ,$E_a$ is the activation energy of the electrical conduction .Fig (2) shows the relation of log $\rho$ against 1000/T for the as-deposited and annealed films at (400,450,500,550) °C in the air.
atmosphere, it can be seen that the as-deposited and heated films have the same behavior of resistivity, that decreases with increasing temperature, but the resistivity of the as-deposited is larger than that of the annealed films, the rate of decrease in $\rho$ in the high temperature region is greater than that in the low temperature region, this result shows that the films are semiconducting in nature. The resistivity of the films decreased about three times than the as-deposited film after heat treatment as shown in Fig.(3) where $\rho$ decreased from (40.4 to 4.5) k$\Omega$.cm. The activation energy is determined from the corresponding slopes of log$\rho$ against 1000/T. Fig(4) shows the dependence of $E_a$ on the annealing temperature, activation energy values are of the order (1.5 -1.11) eV, the structural and activation energy studies support the decrease in $\rho$ due to the improvement in crystallinity of the film which is attributed to the filling of discrete of traps lying at or below the Fermi level, which would increase the charge carrier mobility and decrease in defect levels[18]. The carrier concentration (N) can be determined from Hall effect measurements as found in the previous our letter[19] by using the relation $N=1/eR_H$ where $R_H$ is the Hall coefficient and $e$ is the electronic charge. The result indicates n-type conduction. From Fig. (5) and Fig. (6) it can be observed that the films exhibited electron mobility in the range of 160±10 cm$^2$/vs. and carrier concentration around $(10±3) \times 10^{15}$/cm$^3$, the effect of heat treatment is an enhancement in the free carriers and hall mobility, which is probably due to the donor –acceptor band transition where excess Zn acts as donor and some impurity or defects present at surface and interface of the film acts as acceptor [20]. Fig (7) shows the dependence of the activation energy on the carrier concentration so the decrease in the activation energy leads to increase in the carrier concentration. Similar behaviors were reported by several workers [21]. It can be estimated that the heat treatment has an important influence in the structure and electrical properties of the films.

Conclusions:

ZnS films show hexagonal structure, we studied the influence of annealing on the structure and the electrical properties of ZnS thin films. Results show that heat treatment changed the grain size and decreased
the dislocation density which means decreasing in crystal defects, also the resistivity and the activation energy were decreased, moreover hall mobility and carrier concentration were increased with the heat treatment. It is observed that the heat treatment has an important influence in the structure and electrical properties of the films.

References:
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Fig. (1) XRD pattern for ZnS thin film at (A) as-deposited, (B) t=400°C, (C) t=450°C, (D) t=500°C, (E) t=550°C
Fig. (2) the dependance of the log( resistivity) against $1/T$ (k$^{-1}$) of the ZnS thin films

Fig. (3) the behavior of the resistivity with the temperature (A) for the as-deposited film (B) for the annealed film at 500 °C
Fig. (4) the dependence of the activation energy on the annealing temperature

Fig. (5) The behavior of the Hall mobility with the annealing temperature
Fig. (6) the behavior of the carrier concentration with the annealing temp.

Fig. (7) the dependence of the activation energy on the carrier concentration