The Effect Of Thermal Annealing Processes On Structural, Topographical And Optical Properties Of Manages Sulfide Thin Films

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Abstract—This research used mixture (1:1) Mn (99.99) - S (99.99) (lineage Key, live equivalent to an atomic ratio of each compound) to prepare MnS thin films. After deposition, the thin film was placed in a high-temperature furnace to undergo thermal annealing at different temperatures (As-prepared ,150, and 250) °C. The objective was to explore the effects that the described process had on the thin film's internal structure topographical and optical properties. Atomic Force Microscope (topographic image) showed that the size of the thin films crystals grew with increases in either the thermal annealing temperature.

Furthermore, the crystallization directions of MnS (10.3, 15.3 and 22.8) nm can be clearly observed through an X-ray diffraction analysis, and crystallization strength increased with an increase in the thermal annealing temperature. UV-Vis measure-ement spectra showed that ultraviolet (UV) transmittance intensity decreased with increases in thermal annealing temperature and dwelling time. However, when the thermal annealing temperature reached (As-prepared, 150, and 250) °C or exhibited a high grain size to be around (90, 82) nm.

1. Introduction
Manages sulfide (MnS) is wide band gap energy (3.1) eV [1,2] with group (VII–VI) dilute magnetic semiconductor (DMC) that has potential application in solar selective cantinas, solar cell as window buffer material, sensors, photoconductors, optical mass memories. [3-5]. MnS Films powder can be found in three group VII–VI compound semiconductor crystallize in either cubic (α–MnS or rock salt) or zinc blend (β–MnS)or hexagonal wartzite (γ–MnS) structure[6,7]. MnS thin films can be formed by many thermal evaporation techniques is a partly inexpensive, simple convenient method for layer area deposited and variety of substrates can be used to grow thin films. Number of works has not thermally prepared MnS thin film. However, most of workers have been prepared chemically deposited MnS thin films and the deposition of γ- MnS is not achieved at room temperature[1,5,8].

2. Experimental work
In the present work, MnS prepared of compound from alloy of ratio (1:1) (Mn,S) (lineage key -live equivalent to an atomic ratio of each compound).them the mixture in furnace at a temperature reach up to (1200) and left the sampler inside furnace until it is cool gradually and then flushed sample and extract the broken substance. Grinded substance by Mill specials .figure (1) shows the alloy and powder of (MnS) material.

Fig. (1): Images for powder and the inset alloy

Then the MnS powder has been deposited MnS (from this) alloy by thermal evaporation technique using coating unit in vacuum about(2 × 10^{-5})mbar and put it in a special evaporation molybdenum boat .the rate of evaporation was (23.5nm/min) and the film thickness (400 nm) was measured by interference method .The substrate glass was placed directly above the source at a distance about 18 cm after cleaned the glass and the this film which deposited one study the structural, topography and optical properties of all films (as-prepared, 150, and 250) °C were investigated separately by means of (CuKα) XRD-6000, Shimadzu x-ray diffractometer, Fourier transformation infrared spectroscopy, JEOL (JSM-5600) scanning electron microscopy, Philips CM10 pw 6020 transmission electron microscopy, Angs-trom AA 3000 Atomic Force Microscopy and Cary 100 Conc plus UV-Vis spectrophotometer.
3. Results and discussion

Figure (2) the XRD diffraction analysis of the MnS alloy. These result indicates that the peaks relieve for MnS thin film in a cubic face and there is no any trace of hexagonal face.

![XRD spectra of MnS powder](image)

**Fig.(2)** : XRD spectra of MnS powder

The XRD different pattern of preperd thin films by thermal evaporation technique and deposited on glass than annealing temperature (as-prepared, 150, and 250 °C). Shown in figure (3) it revels the mean peaks at diffraction angle of (29.66°, 29.92°, 29.95°) which is prepared at (As-prepared, 150, and 250) °C respectively, correspond ASTM. All the diffraction peaks in Figure (2,3) are indicates to cubic structure with no trait of hexagonal or other faces.

![XRD spectra of MnS thin films](image)

**Fig.(3)**: Fig.(2) : XRD spectra of MnS thin films which prepared at different annealing temperature(As-prepared, 150, and 250) °C

The average crystalline size of MnS thin films was calculated by using Debye-Scherrer’s formula [1]

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

where D is the mean crystallite size, β is the full width at half maximum (FWHM) of the diffraction line, θ is the diffraction angle, and λ is the wavelength of the X-ray radiation. And fund to be (10.3, 15.3 and 22.8) nm which are prepared at (As-prepared, 150 and 250) °C respectively, which is agreement with the determined AFM in visitation.

AFM images of MnS thin films synthesized at different annealing temperature are shown in Figure (4). MnS thin films dispersed bell-shaped and the grains are homogenous and aligned vertically. By using special software (imager 4.62), the root mean square RMS values of surface roughness and average grain size were estimated and presented in Table (1). The MnS thin film prepared at difference annealing temperature and formed larger particles. The average grain size results (listed in Table) disagree with those estimated from XRD due to the fact that the AFM measurement directly visualizes the grains.

Regardless of the degree of structural defects, while the estimation of particle size by XRD is based on size of defect free volume. In Table (1), it is clearly seen that the root mean square of surface roughness decreases with annealing temperature (150 °C) means delivering of more energy implies a high polycrystalline, but increases with annealing temperature (250 °C) due to a thermal microstrain.

![AFM images of MnS thin films](image)

**Fig.(4)**: AFM images of MnS thin films which prepared at different annealing temperature(As-prepared, 150, and 250) °C
Table (1): Average grain, Roughness density and RMS of thin films which prepared at different annealing temp.

<table>
<thead>
<tr>
<th>Samples °C</th>
<th>Average grain size (nm)</th>
<th>Roughness density (nm)</th>
<th>R.M.S (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>70.01</td>
<td>2.01</td>
<td>2.37</td>
</tr>
<tr>
<td>150</td>
<td>83.92</td>
<td>1.37</td>
<td>1.62</td>
</tr>
<tr>
<td>250</td>
<td>90.82</td>
<td>5.87</td>
<td>6.77</td>
</tr>
</tbody>
</table>

The transmittance (T) characteristic can be toll for analysis thin films. Figure (5) show transmission spectra of MnS thin films is which prepared by thermal evaporation techniques and deposited on glass substrate ,The date is corrected for glass in UV-regain ,the transmission is sharply increases because of the wide of absorbed particle size .Also the Figure (5) that transmission decrease at the different annealing temperature ( as prepared and 150 and 250) °C, the maximum value of transmission (90.15 , 61.23 and 58.88 ), ( as prepared and 150 and 250) °C respectively, can be used a window in solar cell application in the rang to IR in other word this material can be describe is in active material below 550 nm. The optical energy gap of MnS was calculated by the tauc relation [9].

\[ a(hv)^2 = A(hv - E_g)^n (2) \]

Where A is a constant, \( \nu \) is the transition frequency and the exponent \( n \) characterizes the nature of band transition. \( n = 1/2 \) and \( 3/2 \) corresponds to direct allowed and direct forbidden transitions and \( n = 2 \) and \( 3 \) corresponds to indirect allowed and indirect forbidden transitions, respectively.

The curves of \( (\alpha h\nu)^2 \) versus \( h\nu \) were plotted and are shown in Figure (6). The optical energy gap of the deposited MnS thin films by thermal evaporation techniques and deposited on glass substrate were found to be (3.05, 3.19 and 3.4) eV for ( as prepared and 150 and 250) °C respectively, where the \( (E_g) \) increases with increases the annealing temperature this values are in agreement with the values obtained by [1].

![Fig. 5: Optical transmittance of MnS thin films which prepared at different annealing temperature (as-prepared, 150, and 250) °C](image)

![Fig. 6: Plot of \((\alpha h\nu)^2\) versus \( h\nu \) curve of annealed and as-prepared MnS thin films](image)
The refractive index can be found from relation (3)[1], the behavior of refractive index shows in Figure (8) and can be noticed that the refractive index increases with increases in wavelength (375-550) nm and decreases in range (550-1100) nm. Also, it increases with increases annealing temperature

\[ n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}. \]

Where \( R \) is the reflection.

This study employed thermal evaporation to improved and deposit a MnS thin films on glass substrate. By varying the thermal annealing temperatures study explored changes in the thin film’s internal structure and UV emission properties.

The results exhibited influences of differing levels on crystal growth and emission properties when different thermal annealing parameters were applied. The experiment showed that an increase in thermal annealing temperature resulted in gradual growth of crystal size, and when specific parameters were applied, the UV emission intensity increased with the crystal growth. However, when the thermal annealing temperature was at (as-prepared, 150 and 250 °C).

Fig. 7: Reflectance of MnS thin films

This indicates that the thermal annealing process increased the thin film’s internal crystallization and simultaneously enhanced the defects in the thin film and the growth of other crystalline phases

Fig. 8: Reflective index of MnS thin films

Conclusions

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Reference


