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Effect of Thickness on Structural and Optical properties of ZnS:Mn films

Prepared by RF magnetron Sputtering Method

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1- Introduction

The zinc sulfide (ZnS) belongs to the II-VI group of semiconducting material with wide band gap of 3.7eV in the near UV region [1]. ZnS thin film is an important semiconductor material because high refractive index (2.35), high transmittance in the visible range, and high dielectric constant. The reduction of the particle size strongly impacts of crystallinity, structural stability and melting point [2]. The unique properties of the nanomaterial ZnS is believed to have originated from the quantum confinement impacts due to the reduction of band structure into discrete quantum levels as a result, of limited size of the nanoparticles [2]. ZnS is suitable for use as host matrix for a large variety of dopants on account of its broad energy band gap. Doping ZnS with transitional metal ions such as Mn²⁺ is an important aspect to yield different nanostructures. [3]. Also ZnS doped with manganese (Mn) is favourable phosphor which appear best optical properties like high luminescent intensity and narrow emission band[4].

There are many deposition techniques used to prepare ZnS thin film, such as spray pyrolysis, sol-gel deposition, chemical bath deposition, pulsed laser deposition, thermal evaporation, and RF magnetron sputtering [5]. Among these synthesis techniques ,

ABSTRACT

In this study, ZnS: Mn thin films prepared by RF magnetron sputtering technique, were mixed 20 g of ZnS with Mn (2%), and deposited on glass substrate at temperature of 100°C with different thickness (404, 775, and 900) nm. The prepared films were investigated by X-ray diffraction (XRD), atomic force microscopic (AFM), scanning electronic microscopic (SEM), and UV-VIS spectrophotometer. XRD results shows that the films have single crystallization nature with cubic crystal structure (Zinc blende) and strong peaks at (111) as highly preferential orientation. SEM and AFM analysis indicates that the diameter of particles were found to be nanometer, it ranged up to 29.55nm, 89.42nm at thickness (900nm) respectively. The results of UV-Vis spectrophotometry show that the transparency of films with different thickness was found to be around 53.43-86.63% in visible range. The band gap energies are calculated to be between 3.20-3.70 eV.

RF magnetron sputtering method has some advantages such as high film growth rate, easier controllability of the deposition parameters and compatibility with sputtering deposition of absorber and window layer[6]. In this paper, the influence of thickness on structural and optical properties of ZnS: Mn prepared by RF magnetron sputtering technique has been studied.

2 - Experimental:

Radio frequency (RF) magnetron sputtering method used to synthesis ZnS thin film on glass substrate , were mixed 20 g of ZnS with 0.4mg of Mn (99.99% purity) placed in a mold for compressed by the hydraulic piston with pressure (8-10) tons to prepare target of 5cm diameter and thickness 3mm then sintered for 2 hrs at temperature 200°C. The target mounted in the magnetron gun , then close the door of deposition chamber and evacuated to final pressure (7.9×10^{-5} torr) by Dry scroll pump and then , the pressure upto (2.3×10^{-2} torr) by introduction high purity Ar gas (99.99% purity) into deposition chamber [5]. The RF power was 100 watt. The sputtering time was about (1, 2, and 3) hrs during sputtering process; the substrate temperature was maintained at 100°C.

The structural characterization of thin film is determined by X-ray diffraction (XRD), using Braker D2 PH ASER X-ray diffractometer with Cu- α radiation ($\lambda=1.5406 \text{ \AA}$) in 2θ range from 20° - 80° . The surface topographic of thin films deposited on glass substrate has been analyzed by using atomic force microscopy (AA 3000 scanning probe microscope. tib NSC35/AIBS).The shape and particle size were carried out by scanning electron microscopy (SEM) using (Hitachi S-4160) with magnification 100KX. The optical measurements of the thin films were carried out by using (UV-1650PC Shimadzu software 1800 UV-Visible recording Spectrophotometer) in the wavelength range from 200 to 1100 nm at room temperature.

3- The Results and discussion

3.1 XRD analysis:

Figure (1) demonstrated the X-ray diffraction of ZnS: Mn thin film, were it deposited on glass substrate at temperature 100°C with deposition time was set to (1, 2, and 3) hrs corresponding to film thickness of about (404, 775, and 900)nm respectively, by using RF magnetron sputtering under vacuum (2.3×10^{-2} torr). The XRD pattern has one peak observed for thickness (404, 775, and 900) nm at 2θ values 28.7983° , 29.0558° , and 28.7124° respectively, that can belong the (111) diffraction with cubic crystal structure (Zinc blende) of ZnS: Mn which is identical with standard (JCPDS file No:96-500-0089), This is our result agreement with [7,8]. The preferred orientation along (111) direction, indicates that the faces of these nanoparticles are composed primarily of (111) planes. It is observed from figure (1) that the peak intensity is increased with the film thickness from 404 to 900 nm this indicates that (FWHM) of diffraction peaks decrease, as the film is enhance and the particle size become larger with increase of film thickness. This is meaning that the crystallinity of film is improved, as the film thickness increase; this result is in agreement with behavior the previous results [9].

From Full Width at Half Maximum (FWHM) of X-ray diffraction peak is calculated the crystalline size by Debye- sheerer formula [9].

$$D = \frac{k\lambda}{\beta \cos\theta} \dots \dots (1)$$

Where K is a constant ($K=0.94$), is wave length of X-ray ($1.5406 \text{ \AA}$), and β is the full width at half maximum in radians of XRD peak. It is found that the crystalline size of (11.9, 19.1, and 20.5) nm at thickness (404, 775, and 900) nm respectively.

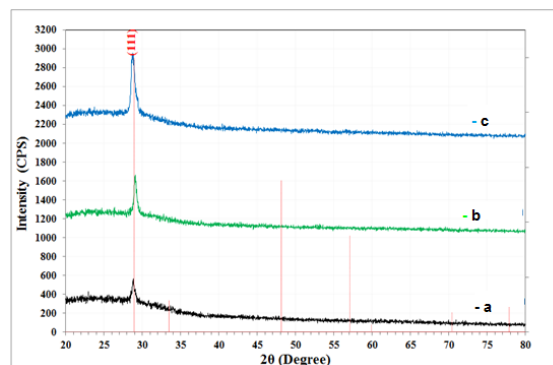


Figure (1): XRD patterns of ZnS:Mn thin films with different thickness (a-404, b-775, and c-900) nm

3-2 Atomic force microscope

The topographic of surface of ZnS: Mn thin films was analyzed using atomic force microscope. Figure (2) shows the typical three dimensional AFM image and granularity cumulation distribution chart of ZnS:Mn thin films prepared by using RF magnetron sputtering technique on glass substrates at thickness of (404, 775, and 900) nm. This figure exhibited that thin film uniformly distributed over the film are high dense structure and is deposited very well. The values of average diameter of grain size and surface roughness for ZnS: Mn thin films are given in table (1). This table displays that average diameter of grain size increasing with increase in thickness. This may be attributed to reasons, first one is the increase in sputtering rate, and secondly is attributed to the possibility of some small grains agglomerated to form grater grains as increasing deposited time with improved crystallinity as observed from the XRD [10].

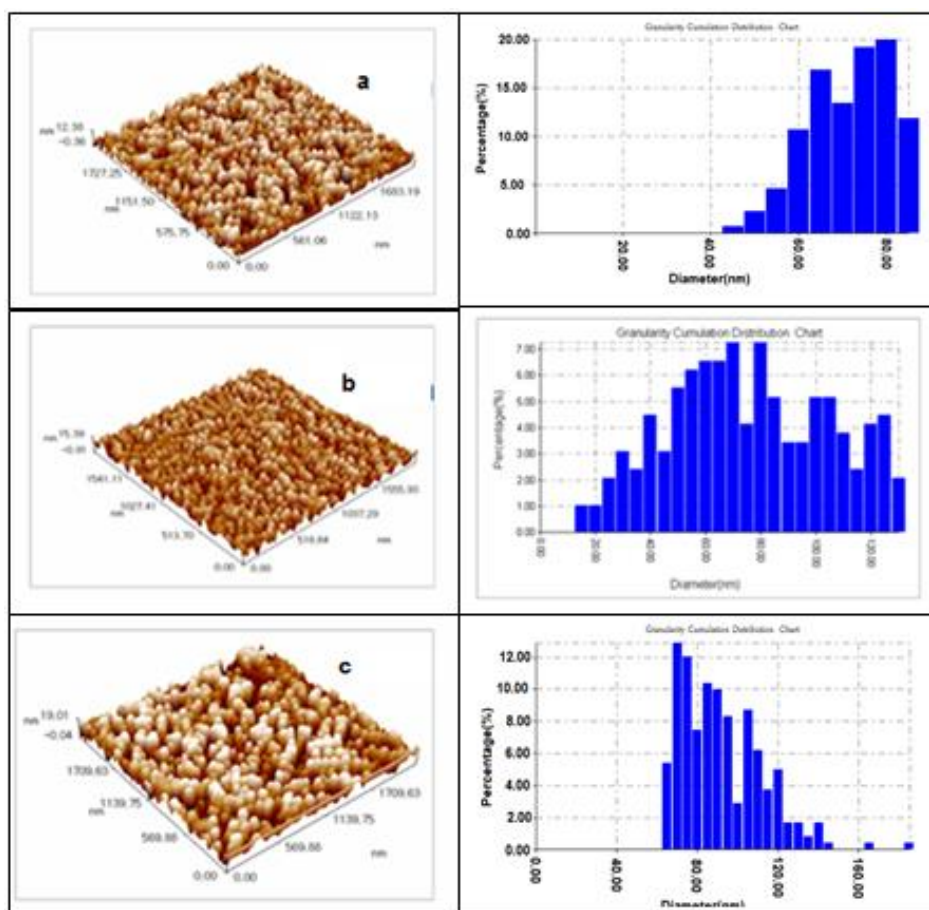


Figure (2): Three dimensional AFM image and granularity cumulation distribution chart of ZnS:Mn thin films with different thickness (a-404, b-775, and c-900) nm.

Table (1): Variation of grain size of ZnS:Mn from XRD, SEM, AFM at different thickness

Deposited time (hrs)	Thickness (nm)	Crystallite size (nm) XRD	Grain Size (nm) SEM	Grain Size (nm) AFM	Roughness (nm)
1	404	11.9	22.92	68.96	3.64
2	775	19.1	24.45	73.27	8.63
3	900	20.5	29.55	89.42	4.55

3-3 scanning electronic microscopy

Figure (3) SEM image with magnification power 100KX, to allow a review of detail growth mechanism of ZnS:Mn with different thickness (404, 775, and 900), by using RF magnetron sputtering . The image clearly exhibits tightly packed grains, furthermore, we can see that the grains having uniform, dense and homogenous distribution. It was observed from SEM Image that the sputtered grains diameter is increased with increasing in film thickness as shown in table (1), and increase of film thickness leads to crate accumulation on grain as islant clusters.

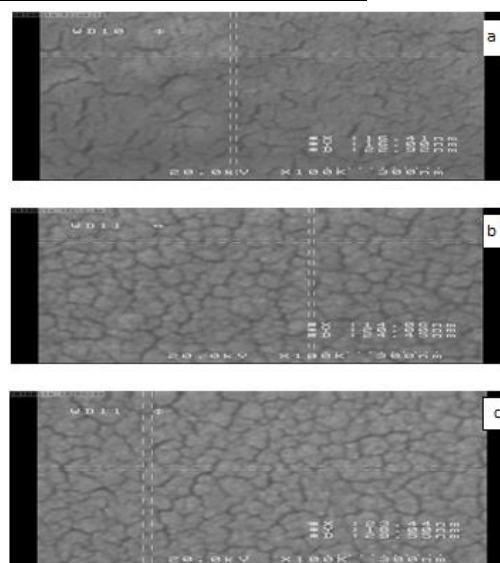


Figure (3): SEM image of ZnS:Mn film at thickness (a-404, b-775, c-900) nm

3-4 UV- Visible spectroscopy:

Optical transmittance for ZnS:Mn film as measured in the range of incident light wave length (200-1100) nm. Figure (4) show transmittance spectra of the deposited film on glass substrate. It has been observed that the transmission of all film decrease with increase in the film thickness, because that the thicker film have more atoms are present in the film so more states which will be available for the photons to be absorbed. The values of transmittance for ZnS: Mn thin film and are measurements at ($\lambda = 550$ nm) as shown in table (2).

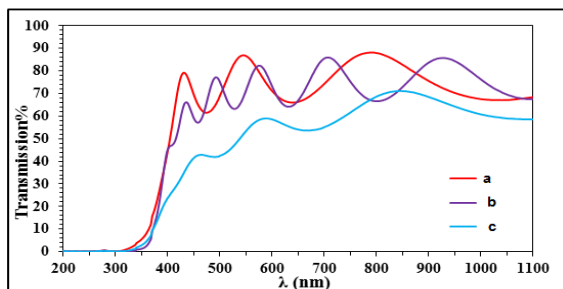


Figure (4) : Variation of transmittance with wavelength of ZnS:Mn thin films at thickness (a-404, b-775, and c-900) nm

Figure (5) show the absorption coefficient (α) as function of wave length for ZnS :Mn at thickness (404, 775, and 900) nm. It can be observed from figure (5) that the absorption coefficient is possess high values at short wave length , then decrease sharply to reach constant value at long wave length above 405nm.

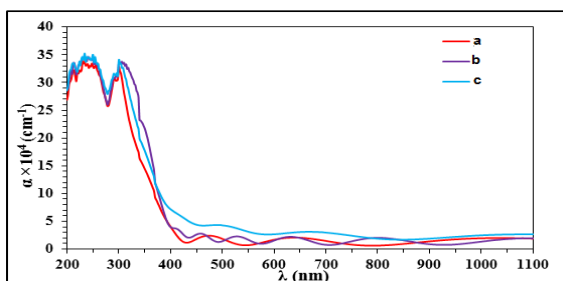


Figure (5): absorption coefficient (α) versus wavelength for ZnS:Mn thin films at thickness (a-404, b-775, and c-900) nm.

From the value of transmission spectra, optical band gap was calculated by using tauc relation [11,12].

$$\alpha h\nu = B(h\nu - E_g^{\text{opt}})^r \dots 2$$

Where B is constant, E_g is band gap energy and $r=1/2$ for direct allowed transition. The band gap value was

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determined by extrapolating straight of the plot $(\alpha h\nu)^2$ versus the $h\nu$ graph on the $h\nu$ -axis. The linear part indicates that the transition mode in this film is of direct nature. The result show that the film thickness is very important in the optical band gap assignment, it is observed that the optical energy band gap is decrease from (3.70 eV to 3.20 eV) with increasing of film thickness from (404 to 900) nm as shown in figure (6) and table (2) , these result are in agreement with [13].

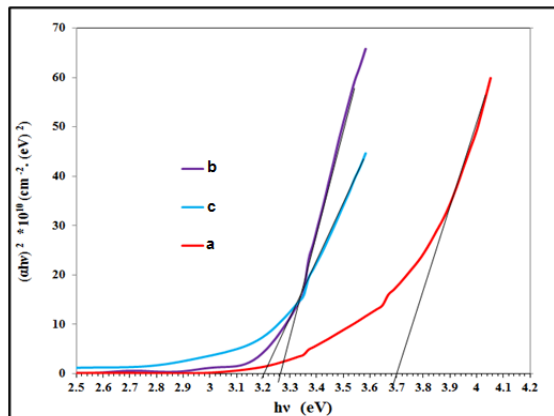


Figure (6): Band gap of ZnS:Mn with different thickness (a-404, b-775, c-900) nm

Table (2): Variation of transmittance, absorption coefficient, and Band gap of ZnS: Mn at different thickness

Deposition Time (hrs)	Thickness (nm)	T% ($\lambda=550$ nm)	α (cm ⁻¹) ($\lambda=550$ nm)	E _g (eV)
1	404	86.63	7174	3.70
2	775	71.38	16858	3.26
3	900	53.43	31344	3.20

Conclusions

ZnS: Mn thin film of thickness (404, 775, and 900)nm deposited on glass substrate at temperature 100°C have been synthesis successfully by RF magnetron sputtering. The XRD analysis of these films at different thickness showed that the structure is single crystalline with cubic structure (Zinc blende) and there are strong peaks at (111) direction, the intensity and crystalline size increases with increase film thickness. The percentage optical transmittance was observed to decreases with increase in film thicknesses in the visible region, also band gap decreases with increases in film thickness.

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تأثير السمك على الخواص التركيبية والبصرية لأغشية (ZnS: Mn) المحضرة بطريقة الترذيد الماكنتروني ذي التردد الراديوي.

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الملخص

تم في هذا البحث تحضير أغشية رقيقة ZnS:Mn باستخدام تقنية الترذيد الماكنتروني، حيث مزج 20g من كبريتيد الخارصين مع المنغنيز بنسبة (2%)، ثم رسبت على قواعد زجاجية عند درجة حرارة 100°C بسماك مختلفة (404, 775, and 900)nm. الأغشية المحضرة درست بواسطة حيود الأشعة السينية ومجهر القوة الذرية والمجهر الكتروني الماسح مطياف UV-vis. أظهرت نتائج حيود الأشعة السينية أن الغشاء يمتلك تركيب مكعب (Zinc blende) من نوع أحادي التبلور ذي الاتجاهية (111). كما أن التحليل باستخدام مجهر القوة الذرية والمجهر الكتروني الماسح أكد لنا بأن القطر للجسيمات هو بحدود النانومتر إذ يتراوح 29.55nm, 89.42nm عند السمك (900nm) على التوالي. نتائج التحليل البصري أكد لنا بأن النفاذية البصرية للأغشية بسماك مختلفة تراوحت بين 53.43-86.63% في المنطقة المرئية. وفجوة الطاقة البصرية تراوحت بين 3.20-3.70 eV.