Structural characterization of gamma irradiated ZnS thin films

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Abstract:

The effects of gamma irradiation on the structure of ZnS films , which preparing by flash evaporation method, are studied using XRD. Two peaks of (111), (220) orientations are appeared in X ray chart indicating the cubic phase of the films .The lattice parameter, grain size, average internal stress, microstrain, dislocation density and degree of preferred orientation in the film are calculated and correlated with gamma irradiation.

Key words: Flash evaporation, ZnS thin films, Crystal quality, Grain size

Introduction:

Deep understanding of the physical properties of the materials under the influence of radiation is of great importance in a wide range of applications including medical imaging, industrial process monitoring, national security and treaty verification, environmental safety and remediation, and basic science. [1] Studies on the changes in optical properties of thin films irradiated with ionizing radiations yield valuable informations regarding the electronic processes in these materials. Ionization occurs and charged species, both ionic and free radical, are formed. It is believed that ionizing radiation causes structural defects (called color centers or oxygen vacancies in oxides) leading to their density change on the exposure to γ-rays.[2]

Nanocrystalline ZnS thin film has received much attention lately because of its probable important role in the photovoltaic technology and its vast application in optoelectronic devices.[3] ZnS has been used in cathode-ray tubes(CRT) and field emission display (FED) phosphors for a long time . It can also be used for electroluminescent devices and photodiodes.[4]

ZnS is ionic crystal; it is strong, brittle material with high melting temperature compared to metals. It has a single diatomic formula unit in the primitive unit cell [5] .It an n type semiconductor, whose band gap was reported to be 3.7 eV. Its constituent elements are nontoxic to the human body, and are very cheap and abundant. Therefore, ZnS is very suitable for a window layer of heterojunction solar cells. [6]

In this work, radiation-induced variations in the structural properties of ZnS thin films are studied

Materials and Methods:

Polycrystalline ZnS thin films were grown on preheated glass substrates up to 100 ^{o}C by flash evaporation technique.

High purity of ZnS (Aldrich company 99.99%) was evaporated by a molybdenum boat filament in a high

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vacuum chamber (pressure about 10^{-6} torr).

During the deposition of ZnS films, the filament and substrate were kept about 10 cm apart, this long distance results in the formation of quite uniform films, prior to deposition, the glass substrate were cleaned aqua – regia and washed in distilled water and isopropyl alcohol. The deposition rate was 0.8 nm/s to obtain films with thickness of a bout 0.5±0.05 μm. Optical and transition spectra were recorded by double beam UV/VIS (Shimadzu Corporation Japan). in the wavelength range (300 -900) nm.

A ^{60}CO gamma – rays used to irradiate the thin films under Investigation.

Results and Discussion:

The thermal evaporated ZnS thin films possess cubic structure. It is confirmed by comparing the peak positions (2θ) of the XRD patterns of the films with the standard X-ray powder diffraction data file (card no. 5-0566). Figure (1) represents the XRD patterns of unirradiated and irradiated ZnS thin film. All films show the most preferred plane [111] in addition to [220] reflections. No other peak beside these is observed which establishes the single phase cubic structure of the films.

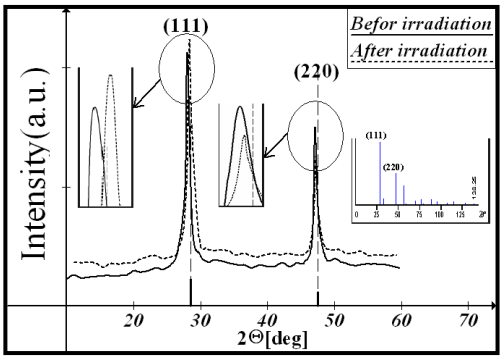

Fig. (1) XRD pattern of irradiated and unirradiated ZnS films. The inset shows

JCPDS File 050566.

It is seen that the peaks are more broadened and shifted to higher diffraction angle when the film is exposure to gamma particles.

The various structural parameters for unirradiated and irradiated ZnS thin films are calculated using the relevant formulas and are systematically represented in table 1.

Table 1. Structural parameters of unirradiated and irradiated ZnS thin films.

Oriantation	2θ[deg.]		Grain Size (nm)		d (nm)		(a) (nm) corrected	
	(unirr.)	(irr.)	(unirr.)	(irr.)	(unirr.)	(irr.)	(unirr.)	(irr.)
[111]	28.09	28.37	12.20	10.79	0.317	0.314	0.537	0.541
[220]	47.22	47.30	-	-	0.192	0.191		
Orientation	Microstrain		Dislocation density $(cm)^{-2}$		Stress GPa			
	(unirr.)		(irr.)	(unirr.)		(irr.)	(unirr.)	(irr.)
[111]	0.00284		0.00321	6.5×10^{11}		8.2×10^{11}	0.871	-0.013

The lattice constant `*a*' for the cubic phase structure is determined by the relation:

$$a = d*(h^2+k^2+l^2)^{1/2}$$

where'd' is the distance between atomic planes, which is calculated by using bragg law.

The corrected values of lattice constants are estimated from the Nelson–Riley plots (figure 2). The Nelson–Riley curve is plotted between the calculated '*a*' for different planes and the error function: **[7]**

$$f(\theta) = 1/2\ ((\cos2\theta)^2/\sin\theta + (\cos2\theta)^2/\theta)$$

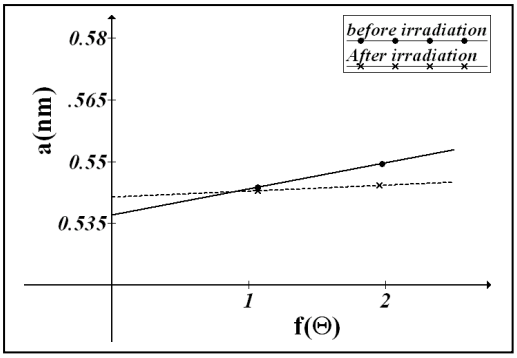

Fig. (2) Nelson–Riley plots for accurate measurement of lattice constants of ZnS films

One very important use of XRD when dealing with nanocrystals is to estimate crystal dimensions through the Scherrer relationship: [8]

$t = 0.9\,\lambda / B\cos\theta$

where **λ** is the X-ray wavelength (**0.154 nm**), **B** is the peak full width at half maximum (FWHM) in radians of peaks, and **θ** is the peak position. Actually, to be more precise, what is measured is not necessarily crystal size but coherence length, the length over which the periodicity of the crystal is complete. It's value before and after irradiation are (**12.2 and 10.79 nm**) respectively for (111) plane . This result is expected because exposure to **γ** particle produced defects which itself reduces coherence length.

Another factor which is responsible (among other things) on the broadening of XRD profile in figure (1) is microstrain . The microstrain (**ε**) developed in the ZnS film is calculated from the relation; [7]

$\varepsilon = (B\cos\theta)/4$,

The change in lattice constant 'as seen above' for irradiated thin film suggests that the film grains are *strained* and that may be owing to the change of nature and concentration of the native imperfections. As shown in table (1), the microstrain increases from **$(2.84*10^{-3})$** to **$(3.21*10^{-3})$** after **γ** irradiation.

A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with that in another part. Dislocation density is defined as the length of dislocation line per unit volume of the crystal. [9]

Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections, i.e. thermodynamic considerations are insufficient to account for their existence in the observed densities. In fact, the growth mechanism involving dislocation is a matter of importance. In the present study, the dislocation density (**ρ**) is estimated from Williamson and Smallman method using the relation [7]

$$\rho = 15\,\varepsilon / a\,t$$

for cubic ZnS thin films. Dislocation density (ρ) increases after irradiation from **6.5×10^{11}** $(cm)^{-2}$ to **8.2×10^{11}** $(cm)^{-2}$. The effect of exposure to gamma ray on the orientation of the polycrystalline films are investigated by evaluating the texture coefficient T_c (hkl) using the following relation [10]

$$Tc(hkl) = \frac{I(hkl)/I_0(hkl)}{(1/N)[\Sigma I(hkl)/I_0(hkl)]}$$

where T_c(hkl) is the texture coefficient of the (hkl) plane, I is the measured intensity, Io is the JCPDS standard intensity and N is the number of diffraction peaks. For [111],T_c (hkl) change from **0.839714** to **1.029** due to irradiation ,but for [220], T_c (hkl) change from **1.16** to **0.97**. The prefer orientation [111] becomes more *dominant* as a result of gamma irradiation. The increase in the texture coefficient of the film with gamma irradiation indicates that a large number of crystallites are oriented along the [111] direction.

All vacuum evaporated films are in a state of stress [11]. The shift of the diffraction peaks' positions from its normal value - see figure (1) - is mainly associated with residual stress in the film [12]. The total stress is

composed of a thermal stress and an intrinsic stress. The thermal stress is due to the difference in the thermal expansion coefficients of the film and substrate material. The intrinsic stress is due to the accumulating effect of the crystallographic flaws that are built in the film during deposition. The average internal stress developed in the films is determined by the relation [13],

$$S = (Y/2\xi)\,(a_0 - a)/a_0.$$

Here **Y** (**76.6 G pa)** and ξ **(0.32)** are the Young's modulus and Poisson's ratio of ZnS film respectively , a_0 **(0.54094 nm)** is the bulk lattice constant of ZnS [14]. The estimated '*a*' refers to the lattice constant perpendicular to the film plane.

S = 0.871GPa. for unirradiated film. **S = -0.013 GPa.** for irradiated one . The average internal stress for unirradiated film is found to be tensile in nature , but it become compressional stress after irradiation. The defects have a probability to migrate parallel to the film surface due to gamma irradiation so that the films have a tendency to expand and develop an internal compressive stress.

Conclusions:

XRD peaks shows a preferred orientation along [111] plane in addition to prominent plane [220], but after irradiation [111] plane become more dominant The shift of the diffraction peaks' positions from its normal value is mainly associated with residual stress in the film which change from tensile to compressive stresses due to increment of the a-axis value in comparison at the a_0 (ASTM) nm. The XRD peaks are more broadened after irradiation due to decrease grain sizes and increase microstrain and dislocation density inside the films.

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تأثير أشعة كاما في الخواص التركيبية لأغشية كبريتيد الخارصين الرقيقة المحضرة بطريقة التبخير الوميضي

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الخلاصة:

باستخدام حيود الاشعة السينية تمت دراسة تأثير أشعة كاما في الخواص التركيبية لأغشية كبريتيد الخارصين الرقيقة المرسبة على قواعد من الزجاج بتقنية التبخير الوميضي الى ظهور القمتين (111),(220) في بطاقة الاشعة السينية دليل على التركيب التكعيبي للاغشية. ثابت الشبيكة ،الحجم الحبيبي ، معدل الاجهاد الداخلي ، المطاوعة المجهرية ، كثافة الانخلاعات ، وكانت المستويات البلورية المتسيدة قد حسبت وربطت بالتشعيع باشعة كاما.