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Influence Of Structural Properties Of Pure SnO_2,Fe_2O_3 And Nanocomposite SnO_2 /Fe_2O_3 Thin Films Deposited By Spray Pyrolysis Technique

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***Abstract*—In this study, nanocomposite Fe_2O_3/SnO_2 films have been successfully deposited on glass substrates by chemical spray pyrolysis (CSP) technique at substrate temperature of (400˚C), and the thickness of the prepared films were about (300nm), and different composite consentration (20, 30, 40 and 50%). The XRD results showed that (pure SnO_2-Fe_2O_3, 20, 30, 40 and 50%) films are polycrystalline in nature with Tetragonal structure and preferred orientation along (110) plane, while the pure Fe_2O_3 film is polycrystalline in nature with Hexagonal structure and preferred orientation along (104) plane. The crystallite size was calculated using Scherrer formula. The crystallite size of the samples was maximum (25.88nm) at pure Fe_2O_3, and it was minimum (2.05nm) at (70%SnO_2/30%Fe_2O_3) nanocomposite thin film.**

Keywords—SnO_2 ,XRD , nanocomposite , number of layers, texture coefficient,

1. Introduction

Nano-crystals of semiconductor metal oxides have attracted a great interest due to their intriguing properties, which are different from those of their corresponding bulk State [1]. Crystal structures are usually determined by the technique of x-ray crystallography. This technique relies on the fact that the distances between atoms in crystals are of the same order of magnitude as the wavelength of x-rays (of the order of 1 Å or 100 pm): a crystal thus acts as a three-dimensional diffraction grating to a beam of x-rays [2]. One of the most promising materials in this regard is tin dioxide, SnO_2 is a remarkable n-type semiconductor material having wide band gap (3.6 eV) and is sought for a wide variety of applications. It has been used, for example, as solid state sensor mainly due to its sensitivity towards different gaseous species [3,4], photovoltaic energy conversion [5], to make indium tin dioxide (ITO) transparent conductive thin film coatings [6], solid-state gas sensors [7], transparent conducting electrodes [8], rechargeable Li batteries [9], and optical electronic devices [10]. Fe_2O_3 is one of the most important transition metal oxides with a bandgap of 2.2 eV. It received an extensive attention due to its good intrinsic physical and chemical properties, such as its low cost, stability under ambient conditions, and environmentally friendly properties [11] .Due to these properties, Fe_2O_3 nanostructures can have wide applications in many fields including magnetic recording materials, catalysis, optical devices, gas sensors, photochemical and pigments [12]. For a long time, composite materials of semiconductors have been studied extensively owing to their unique optical and electric properties [13-16]. Their composites also attracted great attention owing to their stable, outstanding gas-sensitive properties and potential application in Li-ion battery electrode[17-19]. Although some groups have synthesized and studied thin films and nanopowders of SnO_2/Fe_2O_3 composite [17,18]. The aim of the study is to prepare SnO_2/Fe_2O_3 nanocoposite films on glass substrate by chemical spray pyrolysis technique and to study the effect of the composite concentration on the structural properties of these films. The structure properties will include the X-rays diffractions such as measuring: the lattice constant ,grain size ,FWHM ,lattice spacing ,texture coefficient, Number of layers ,dislocation and number of crystalline per unit area.

2.Experimental

Firstly prepared the Fe_2O_3 pure from hematite chloride Hydrated ($FeCl_3.6H_2O$) diluted with distilled water, in order to prepare the solution of 0.1 molar concentration from these material, 0.811 gm weight of ($FeCl_3.6H_2O$), melted in 50 ml of distilled water Secondary prepared the SnO_2 pure from 0.1M concentration precursor solution of the pure Stannic Chloride Hydrated, it chemical symbol ($SnCl_4.5H_2O$) by Purity 99.9, molecular weight (350.58g / mol), it has been prepared by dissolving a solute quantity of 1.753g of $SnCl_4$ in 50 ml of distilled water. The both solutions were added into a round-bottom flask with stirring. SnO_2/Fe_2O_3 nanocomposite with different SnO_2 and Fe_2O_3 contents were deposited on a glass substrate by spray pyrolysis technique under ambient atmosphere. Two kinds of aqueous solution, Stannic Chloride $SnCl_4$ and Hematite Chloride $FeCl_3$ were chosen as the sources of Stannic and Hematite respectively. In order to obtain SnO_2/Fe_2O_3 nanocomposite with different contents see Table 1. The deposition parameters were the same for the series of SnO_2/ Fe_2O_3 films. The pure Stannic Chloride $SnCl_4$, pure Hematite Chloride $FeCl_3$ and distilled water were mixed thoroughly to get the solution with a concentration of 0.1 M. the substrate temperature was set at 400°°C during the film growth.

Table 1: the percentage of SnO_2 and Fe_2O_3.

percentage	SnO_2	Fe_2O_3
Pure -SnO_2	100	Zero
20%	80	20
30%	70	30
40%	60	40
50%	50	50
Pure-Fe_2O_3	Zero	100

Thickness (t) of the samples was calculated using the weighting method, by using the relationship

$$t = \frac{\Delta m}{A.\rho}. \qquad (1)$$

Where (t) is the thin film thickness, (Δm) is the change in weight (The difference between the substrate weight before and after the deposition), (ρ) The density of the thin film material (the density of Ferric oxide material equal to 5.24g /cm^3, Tin oxide material equal to (6.95 g/cm^3), and (A) substrate surface area equal (625cm^2). where the use of the thickness of (300nm). The structure of SnO_2/Fe_2O_3 nanocomposite thin films were examined by X-ray diffractions using a(XR-DIFRACTOMETER/6000) type Shimadzu X-ray diffractometer system.

3. Results and discussion

The XRD spectra of SnO_2/Fe_2O_3 nanocomposite films prepared by chemical spray pyrolysis technique at substrate temperature of (400 ^oC°C) has been shown figures (1), (2) and (3).

XRD pattern of SnO_2 thin film shown in figure (1). The presence of diffraction peaks indicates that the film is polycrystalline with a tetragonal structure. It is revealed that the sprayed film has peaks corresponding to (110) directions of tetragonal SnO_2 crystal structure which is corresponding to the position $2\theta=$ 26.7937° , Figure (2), shows the x-ray diffraction (XRD) pattern of pure Fe_2O_3 thin films are polycrystalline structure of hexagonal wurtzite phase. The preferential orientation of the crystallinity with the prominent (104) peak at $2\theta=33.1492°$, this results are agreement with the Joint Committee of Powder Diffraction Standard (JCPDS card, No.41-1446 and card, No.41-1445).

The X-ray diffraction data revealed that the crystallinity of the films depended strongly on the Fe_2O_3 concentrations in the thin film, shown in figure 3 (a,b) that XRD of ($80\%Fe_2O_3/20\%SnO_2$), and ($70\% Fe_2O_3/30\%SnO_2$) nanocomposite that show decrease in (110) , (101) and (211) peaks intensity and shifted toward decrease 2θ while the other peak (211) are appear . The XRD patterns show only peaks consistent with the SnO_2 phase with no indication of any secondary Fe_2O_3 structure or any impurity phases.

The intensity of (110) peak shows strong decrease for ($60\% Fe_2O_3/40\%SnO_2$) as shown in Figure 3 (c). and in this case shows a new peak was appeared (116) for Fe_2O_3.

Figure 3 (d) shows XRD of ($50\% Fe_2O_3/50\%SnO_2$) nanocomposite thin film it recognized a large effect on the structure, the intensity of other peaks (101) and (112) decrease and increase in the intensity of (116) peak, and show a new peak was appeared (012) for Fe_2O_3.

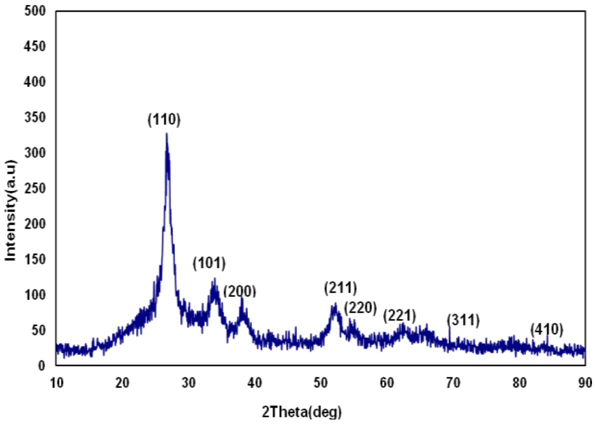

Fig. 1: XRD pattern of SnO_2 pure deposited on glass substrate.

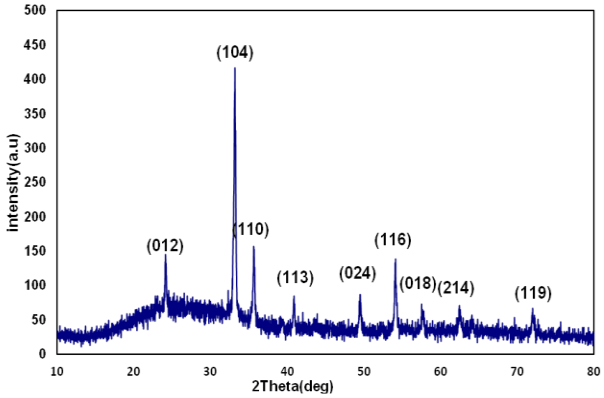

Fig. 2: XRD pattern of Fe_2O_3 pure deposited on glass substrate

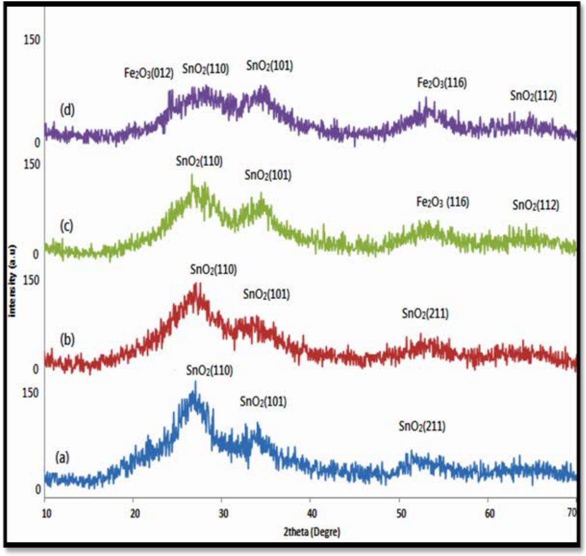

Fig.3 : XRD pattern (a) 80% Fe_2O_3/ 20%SnO_2,(b)70%Fe_2O_3/30%SnO_2 , (c) 60% Fe_2O_3/40%SnO_2 , (d) 50% Fe_2O_3/50%SnO_2 nanocomposite deposited on glass substrate

The lattice constants (a_o, c_o) were calculated using the following relations: For tetragonal systems :[20]

$$\frac{1}{d^2}=\frac{h^2+k^2}{a_o}+\frac{l^2}{c_o} \qquad (2)$$

and for hexagonal systems:[21]

$$\frac{1}{d^2}=\frac{4}{3}\left[\frac{h^2+hk+k^2}{a_o}\right]+\frac{l^2}{c_o{}^2} \qquad (3)$$

Where (d) is the interplanar distance, (hkl) are the miller indices and (a_o, c_o) are the lattice constant.

The lattice constant (a,c) for the prepared pure SnO_2, Fe_2O_3 and SnO_2/Fe_2O_3 nanocomposite films at different composite concentration are shown in Table (1), from the Figures (1), (2) and (3).

Table 1: Structure properties of pure SnO_2, Fe_2O_3 and SnO_2/Fe_2O_3 nanocomposite thin films at different composite concentration

sample	(a_o)(Å)	(c_o) (Å)
SnO_2	4.732	3.198
80%Fe_2O_3/20%SnO_2	4.7308	3.190
70%Fe_2O_3/30%SnO_2	4.7376	3.182
60%Fe_2O_3/40%SnO_2	4.7320	3.183
50%Fe_2O_3/50%SnO_2	4.7376	3.180
Fe_2O_3	5.038	13.752

Table 2: Results of X-rays diffraction of SnO_2/Fe_2O_3 nanocomposite.

Sample	2θ (Deg.)	FWHM (Deg.)	hkl	D (nm)	T_c	N_l	δ $x10^{15}m^2$	$N_o x10^{16}m^2$
SnO_2 Pure	26.7937	2.158	(110)	3.8	3.71	205.8	66.2	34.1
80%SnO_2/20%Fe_2O_3	26.498	2.5	(110)	3.26	2.13	214.4	93.8	57.7
70%SnO_2/30%Fe_2O_3	26.5483	4.05	(110)	2.05	2.0	195.1	237.7	231.8
60%SnO_2/40%Fe_2O_3	26.8478	3.1	(110)	2.63	1.21	151.8	144.1	109.4
50%SnO_2/50%Fe_2O_3	26.4478	2.21	(110)	3.71	0.93	101.2	64.1	32.4
Fe_2O_3 Pure	33.1492	0.3115	(104)	25.88	3.78	25.3	13.1	0.094

The scherrer formula is used to determine the grain size and it is increased with increases composite concentration as shown in the Figure (4) and Table (2). The grain size increases from (3.8-25.88) nm as the composite concentration increased from (0- 100%) and according to the dominant peaks.

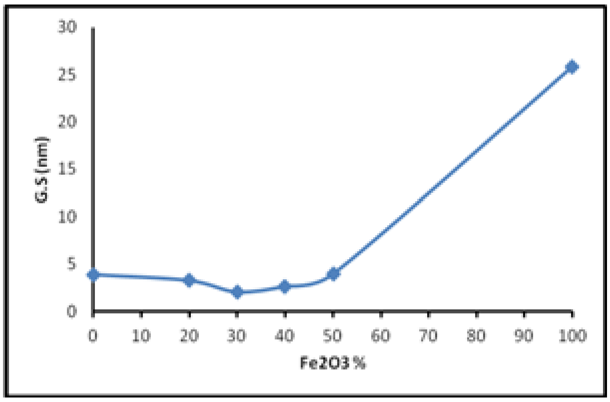

Fig.4 : represents grain size variation with Fe_2O_3 concentration.

Texture Cofficient (Tc)

Texture coefficient (T_C) of SnO_2/Fe_2O_3 nanocomposite films are recorded in Table (2), to describe the preferential orientation, the texture coefficient (T_c) is calculated using relation [22].

$$T_C(hkl) = \frac{I(hkl)/I_0(hkl)}{N_r^{-1}\sum I(hkl)/I_0(hkl)} \qquad (4)$$

Where (I) is the relative intensity. (I_o) is the ASTM relative standard intensity. (N_r) the number of reflections. (hkl) Miller indices.

The texture coefficient T_c is a positive number and have the values: If $T_c \simeq 1$ for all the (hkl) planes considered, then the films are with a randomly oriented crystallite, this is observed in the concentration 60% SnO_2/40% Fe_2O_3 and 50% SnO_2/50%Fe_2O_3, while value higher than 1 (as in the rest of concentration) indicte the abundance of grains in agive (hkl) direction, As show in Figure (6) .

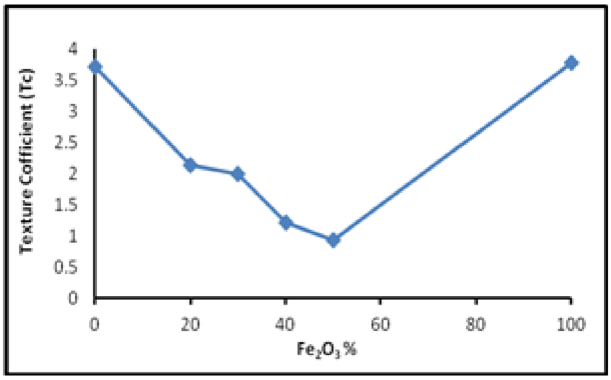

Fig. 6: Texture coefficient variation with Fe_2O_3 concentration.

Number of Laery (N_l)

The number of layers valued from different percentage of SnO_2 and Fe_2O_3 is recorded in Table (2). The number of layers is calculated using the relation [23].

$$t = D \times N_l \qquad (5)$$

Where (D) is a mean crystallite size.

The value of the number of layers decreases with increase Fe_2O_3 ratio as show in Figure (7).

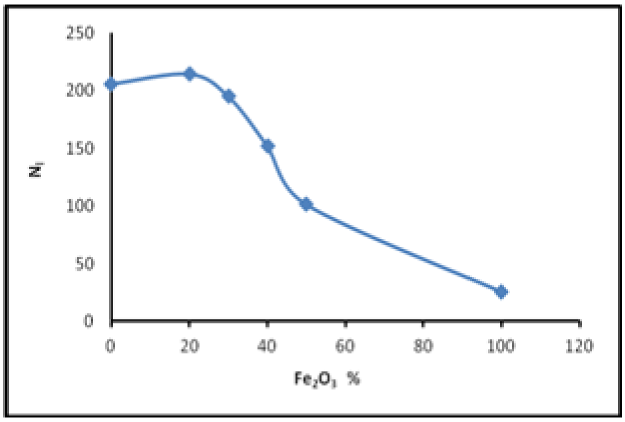

Fig.7: Number of Laery variation with Fe_2O_3 concentration.

Dislocation Density (δ)

The dislocation density is the measure of amount of defects in a crystal calculated using the equation [24]:

$$\delta = 1/D^2 \quad (\text{lines/cm}^2) \qquad (6)$$

It was obtained in the present work confirmed good crystallinity of the nanocrystalline SnO_2/Fe_2O_3 films fabricated by employing spray pyrolysis technique as shown in Table (2).

Number of Crystals (N_o)

The Number of Crystals (N_0) of the SnO_2 /Fe_2O_3 nanocomposite thin films are determined from equation [25]:

$$N_o = t/D^3 \quad (m)^2 \qquad (7)$$

Found that the numbers of crystals per unit area are decreased with increasing of Fe_2O_3 concentration, because the number of crystals is inversely proportional to the cube of the average grian size, the number of crystallites per unit area was calculated and listed in Table (2).

4. Conclusions

The SnO_2/Fe_2O_3 nanocomposite thin films with different Fe_2O_3 concentrations (20,30,40,50,100)% prepared by chemical spray pyrolysis method at substrate temperature of (400 °C) on glass substrate. The XRD results showed that (Pure SnO_2, 20, 30, 40 and 50) % were polycrystalline in nature with a Tetragonal structure and a preferred orientation along (110) plane. A decrease in the values of the crystallization was noticed by the increase of the Fe_2O_3 cncentration, while the pure Fe_2O_3 has been crestalized in a hexagonal wurtzite with the preferred orientation along (104) .The average grain size for SnO_2/Fe_2O_3 nanocomposite thin films, estimated from XRD analysis. The Pure Fe_2O_3 films has highest grain size of about 25.88nm, and the (70%SnO_2/30%Fe_2O_3) nanocomposite thin film has minimum grain size of about 2.05nm.

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