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Effect the Composition Ratio of Cobalt Oxide on the Structural and Optical Properties of Tin Oxide

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ABSTRACT:

Tin oxide thin films were deposited on glass substrate at (400 ºC) by using chemical spray pyrolysis technique and its composed with cobalt oxide in different ratio. The structural, morphologic and optical properties of thin films are investigated by: (XRD) X-Ray Diffraction, (AFM) Atomic Force Microscopy, (UV-Vis)Ultraviolet – Visible Spectroscopy. XRD patterns indicate that the structure of tin oxide thin film is tetragonal. All prepared films were nano materials as stated by Scherrer equation. It might have been found by AFM analysis, those surface roughness increase with increasing of cobalt ratio. By provision about Tauc plots, optical band gaps for thin films are suggested on a chance to be (4.51-2.75) eV

KEYWORDS : Nano composites; thin films; chemical spray pyrolysis, semiconductors.

1.Introduction

Semiconductor thin films are attractive to allow unlike electronic applications (Fay, S., et. al., 2005 - Nishii, J., et. al.2003).Transparent conducting oxides have been a study for ages (Kikuchi, N., et. al., 2013 - Wohlmuth, W. & Adesida, I., 2005). Tin oxides are very important because of a naturally non-stoichiometric prototypical transparent conducting oxide. It has a wide band gap a bout (3.6 eV), , it can be used as a P-type and N-type semiconductor when it was doped (Wu, T .H., et., al., 2006)(Cao, H., et., al., 2006). Doping tin oxide with chlorine, fluorine, cobalt, etc. (Thangaraju, B. 2002)(Abass, A.K. 1987) as donor impurities produce films with a low sheet resistance (Chopra, K., et., al., 1983). Tin oxides films were used as transparent electrodes in display devices as liquid crystal displays (LCDs) and as transparent energetic layers in tin oxide silicon solar cells (Chaudhuri, U. R., et., al., 1990), antireflection coatings, thin films resistors, photochemical devices and electrically conductive glass (Afify,H .H., et., al., 1996).

Cobalt oxide (Co_3O_4) thin films have attracted research attempt in recent ages because of their potential application in different technological fields. It can be used as high temperature solar selective absorbers (Barrera ,E., et., al., 2005), negative electrodes in lithium-ion batteries (Huang ,X.H., et., al., 2008) and anodic electrochromic materials in smart window devices (Shaju, K.M., et., al., 2007). Thin films were prepared by different techniques such as chemical vapor deposition (Kandalkar, S.G ., et., al., 2007), atomic layer deposition(Klepper, K.B., et., al., 2006), sol-gel process(Bahlawane, N., et., al., 2004), RF magnetron sputtering, pulsed laser deposition (Svegl F., et., al., 2000), co-precipitation method, chemical bath deposition and chemical spray pyrolysis. Among these deposition techniques, chemical spray pyrolysis has various benefits: flexibility, ability for preparing nanostructure thin films, low cost and convenience for large deposition area. This technique has been used effectively to produce a variability of porous materials for electrochromic devices such as Fe2O3, WO3, CeO2 and Co3O4 (Dghoughi L., et., al., 2006).

The purpose of paper is enhancement performance of semiconductor tin oxide by preparation thin films of new nano semiconductor in the form of composites with cobalt oxide with a different composition ratio by chemical spray pyrolysis.

1. Experimental

Thin films were grown-up onto glass substrates, using a typical spray pyrolysis unit as shown in Figure 1.

2.1 Preparation of tin oxide:

Tin dioxide thin films were prepared by using tin (II) chloride dihydrate ($SnCl_2.2H_2O$) with molarity concentration solution (0.2M). the weight of ($SnCl_2.2H_2O$) equal (4.5126 g) which calculated by the following equation:

$$M = \frac{wt}{M.wt} \times \frac{1000}{V} \qquad \ldots\ldots\ldots\ldots(1)$$

Where (M) the molar concentration (0.2M), (wt) weight of tin (II) chloride dihydrate, (M.wt) molecular weight of tin (II) chloride dihydrate, (V) volume of deionized water equal to 100 ml.
Then it was dissolved with (20 ml) of ethanol completely dissolved and then completed the volume to (100 ml) with deionized water, and adding a few drops of HCl acid to increase the transparency of the solution. Then the solution was

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mixed and heated to (60°C) using a heater and a magnetic stirrer for 15-20 min to ensure that the material was fully dissolved.

2.2 Preparation of cobalt oxide:

Cobalt oxide thin film was prepared by using cobalt(II) chloride hexahydrate (CoCl2.6H2O). From the same equation, it found that the weight equal (4.7586 g), where the same method of preparation described above was followed.

2.3 Preparation of composites:

Composites thin films were prepared by mixing the two solutions by different volumes ratio as shown in table1.

Table1: Volume ratios of the composites thin films

Sample	$SnCl_2.2H_2O$ (V %)	$CoCl_2.6H_2O$ (V %)
Compos 1	75	25
Compos 2	25	75

2.4 Deposition set-up:

The spray process was carried out by the atomizer, which is 30 cm away from the glass substrate placed on the electrical heater surface. The glass substrates were heated to (400 °C) for films deposition by an electrical heater. The spray process was initiated when the temperature was reached to (400 °C), where the spray time was (5 sec), the number of sprays was (40) and the time which separating between sprays was (1 min). The crystal structure and crystallinity of tin oxide and their composites were determined using an (XRD-6000 Shimadzu X-ray diffraction diffractometer) with Cu-Kα radiation (k =1.5406 A ˚).Surface roughness level of the films was determined using an SPM AA3000/ Angestrom advanced and MIRA3,TESCAN. The absorption spectra of films were recorded using a PC 1650,Shimadzuultraviolet–visible (UV–Vis) spectrophotometer.

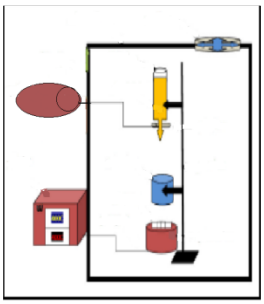

Figure 1: spray pyrolysis system

3. Results and Discussion

3.1. Structural characterization:

X-ray diffraction technique was used to study the structural and crystallinity of prepared thin films as shown in Figures (2-4). It was noted that the peaks correspond to the tetragonal of tin oxide thin film (Vidhya, S., et al., 2016) and the spinal family of composites thin films. The intensity of the peaks was increase with increasing of cobalt ratio, indicating that the crystallization process improves when cobalt is added.

The average crystalline size of thin films was calculated by Scherrer's equation (Hassan, A. I. & Maki, S. I., 2015).

$$D = \frac{k*\lambda}{\beta 1/2 \ cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where D is the average crystalline size, K is Scherrer's constant (0.9), λ is the X-ray wavelength of (1.54 °A), $\beta_{1/2}$ is the FWHM and θ is the Bragg diffraction angle. The microstructural constants of the strong three peaks were show in table 3.

Table 3 explains that the crystalline size of composites was increased with increasing cobalt ratio. This increase helps in the crystallization process, improves the growth of grains and decrease the grain boundaries, ie, removal of crystalline defects and improvement of crystalline material (John, I., et., al., 2014).

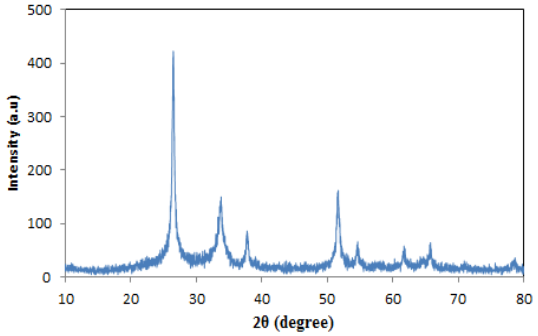

Figure 2: XRD diffractogram of SnO_2

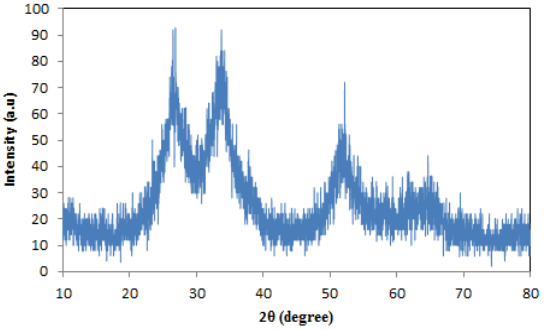

Figure 3: XRD diffractogram of compos 1

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Figure4: XRD diffractogram of compos 2

Table 3: Average of crystallite size

Sample	Average of crystallite size (nm)
SnO_2	21.6986
Compos 1	66.1502
Compos 2	88.9739

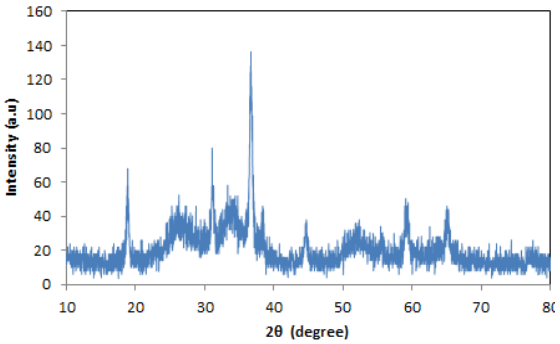


Table 2: Microstructural constants of thin films

Sample	2θ	hkl	d (observed)	d (calculated)	Dp	Dislocation density	No. Unit cell
SnO_2	26.5205	1 1 0	3.35826	3.3570	19.14848	0.002727	10422.24
	34.3385	1 0 1	2.60946	2.6084	14.67505	0.004643	4691.335
	52.2872	2 1 1	1.74821	1.7475	23.26745	0.001847	18698.4
Compos 1	26.5483	0 2 0	3.35481	3.3535	4.693337	0.045398	153.4628
	33.0798	0 1 3	2.70582	2.7048	5.846279	0.029258	296.6175
	33.8989	1 2 1	2.64229	2.6413	5.219644	0.036704	211.0963
Compos 2	18.9162	1 0 1	4.68762	4.6858	21.52997	0.002157	14814.53
	31.1519	0 0 3	2.86874	2.8676	21.0251	0.002262	13796.6
	36.7189	1 2 1	2.44557	2.4446	17.68979	0.003196	8217.248

3.2. Surface characterization:

The surface structure of tin oxide and their composites was studied by AFM technique. The images of AFM for these thin films shown in figures (5-7). The increase of cobalt ratio leads to the raise of the surface roughness slimly because of the different mobility of tin and cobalt atoms, as shown in table 4.

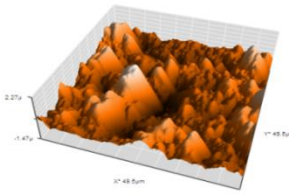
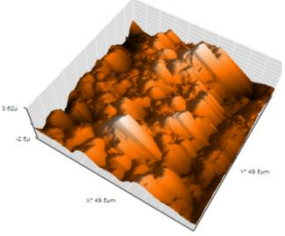


Figure6: (AFM) micrograph of compos 1



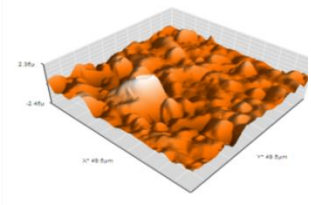


Figure5: (AFM) micrograph of SnO_2

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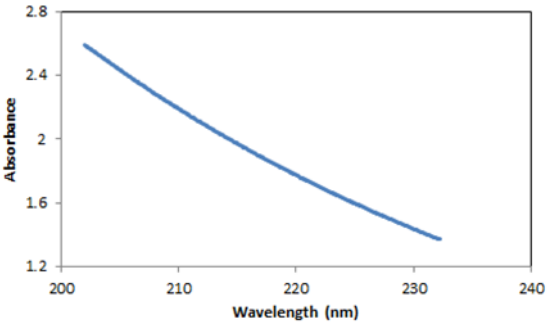

Figure10: Electronic spectrum of compos 2

3.3.2. Energy gap:

The electronic spectra were shown in figures (11-13) were used to extract the optical band gaps of SnO_2 and their composites. The absorption coefficient (α) can be calculated by the following equation (Yousif, S. A. & J. M. Abass, 2013) .

$$\alpha h\nu = B\,(h\nu - Eg) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Hence (α) the frequency of the light, (B) constant value depends upon the type of transition and (n) refers to the number that take certain values as (1/2, 2, 3 and 3/2), these values depend on the type of transition which direct-allowed, direct-forbidden, indirect-allowed or indirect-forbidden. The draw of $(\alpha h\nu)^{1/2}$ against (hν) shows a direct section demonstrating that transitions must be indirectly allowed transitions. The energy gap can be determined by the intercept on the energy axis. Table 6 shows the values of the energy gap of the direct transitions of thin films, with a value (4.6 eV) for tin oxide, and this value is consistent with previous studies (Hassan, A. I. & Maki, S. I., 2015), (Muthana Abd-Alkadum M., 2014). Note that the composites decrease with the increasing of the cobalt ratio. This means that the increasing in the formation of composites led to the

displacement of the absorption edge towards the low energies, where the shortage in the energy gap indicates the emergence of new top levels below, The conductivity, respectively, within the restricted gap led to this decrease in the values of the gap and this behavior is consistent with the researcher (Yousif, S. A. & J. M. Abass, 2013).

Figure 7: (AFM) micrograph of compos 2

Table 4: Roughness of films according to AFM technique

Sample	Surface roughness(nm)
SnO_2	306.58
Compos 1	262.13
Compos 2	767.51

3.3. Optical characterization:

3.3.1. Electronic Spectra:

The electronic spectra of tin oxide and composites were explained by the figures (8-10). The electronic spectra were done by glass substrate as a reference. It can be recognized that the absorption decreased with increasing wavelength and increased with increasing cobalt ratio. This shows that cobalt levels have permeated the self-beams and led to the formation of new prohibited beams (Chowdhury, F.R., et., al., 2011)

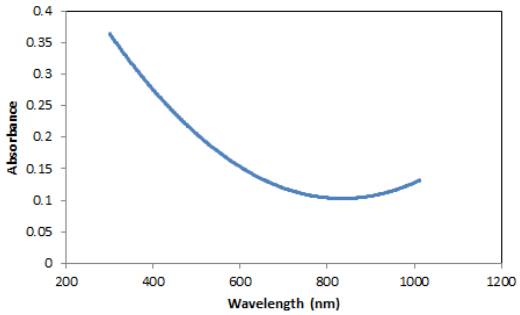

Figure8: Electronic spectrum of SnO_2

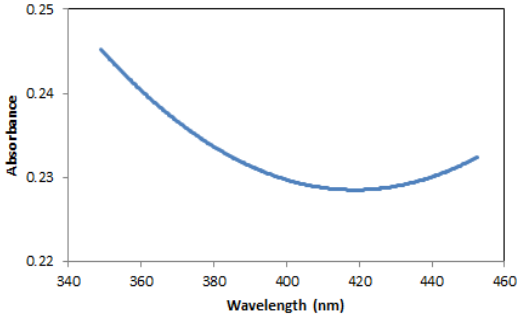

Figure9: Electronic spectrum of compos 1

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cobalt ratio. The electronic spectra were recognized that the absorption decreased with increasing in wavelength and increased with increasing in cobalt ratio. The band gaps with allowed indirect type were decreased as cobalt ratio increase.

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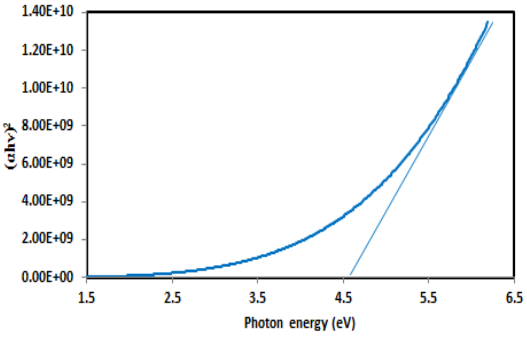

Figure 11: Energy gap of SnO_2

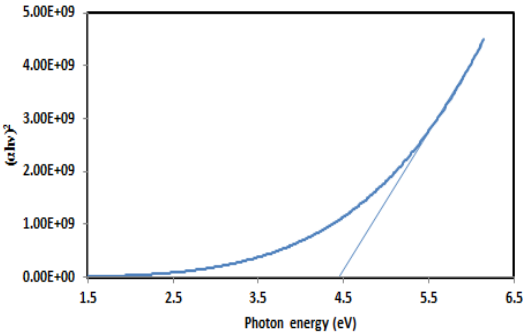

Figure 12: Energy gap of compos 1

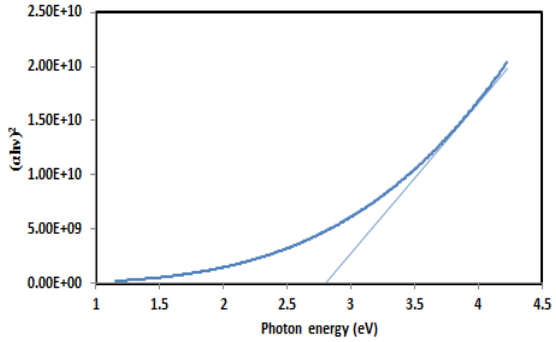

Figure 13: Energy gap of compos 2

Table 7: Value of energy gaps of thin films

Sample	Eg (eV)
SnO_2	4.51
Compos 1	4.49
Compos 2	2.75

4. Conclusion

Compositional Characterization of tin oxide, and their composites thin films were explain that all these thin films were polycrystalline and the structure of SnO_2 was tetragonal. According to Scherrer equation in XRD analysis the average crystallite sizes were decreased by increasing

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