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Preparation composite thin films of tin oxide with cobalt oxide and study their structure and optical characteristics

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[b]Sura A. Abd Al-Hassan,[a] Ahmed K. Abass

[a] Department of Chemistry, College of Science, University of AL-Qadisiyah, Iraq

E-mail: Ahmed.Kadhim@qu.edu.iq

ABSTRACT:

Both tin oxide, cobalt oxide and their composites thin films were deposited on a microscopic slid glass substrateat (400 ºC) utilizing chemical spray pyrolysis technique. The investigation the structural and optical characteristics of thin films were completed by many techniques such: Dispersive Spectroscopy (EDS), Energy X-Ray Diffraction (XRD), Field Emission- Scanning Electron Microscopy (FE-SEM), and Ultraviolet – Visible Spectroscopy (UV-Vis). The peaks of XRD show the crystallinebehavior of the films.The structure of SnO_2 is tetragonal while the structure of Co_3O_4 is cubic. According to Scherrer equation in XRD analysis,all films which prepared to be nano materials. Thepresencesof securing oxygen, cobalt and tin segments with distinctive atomic and weight proportions for cobalt also tin were approved by EDS. FE-SEM images relate the homogenous films as thickly stuffed nano particles.. Optical band gaps of films are calculatedusingTauc plots, which are (4.5-2.5) eV.

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

1.Introduction

Thin film technology is one of the most important technologies that have a major role in the development of semiconductor materials, where it gave a clear idea for a lot of their physical and chemical properties (K. L. Chopra, 1985). It has been widely used in recent years in many applications including photovoltaic stimulation, solar cell, gas sensor and other applications (Perednis, D. and L. J. Gauckler, 2005), (Jeyaprakash, B., et al. 2010). The term of thin films is used to describe one or more layers of substance, that the thickness does not exceed 1 micron (Kotsikau, D., et al. 2004), (H. Bach and D. Krause, 2003). Solid matter becomes a thin film when prepared in layers on solid bases in physical or chemical reactions (S. M. Sze, 1990). Solid bases are based on the nature of the study and using, such as: glass, silicon, aluminum, quartz and others (K.L. Chopra, 1969), (R. A. Smith, 1979).

Semiconductors are used extensively in electronics, but in electronics, optical these materials have some constraints. To overcome this constrains the oxides metals transition are using (Sajeesh, T., et al. 2012), (Hassan, A. I. and S. I. Maki,). The transition metal oxides have a variety structure and characteristics, so it attracted the attention of many researchers in recent years in the field of its applications of scientific and technological (S.Mahajan, et.al.2008). Thin films of semiconductors oxides required for a lot of electronics and optical devices as well as some applications such as the paint, thermal mirrors and photo stimulation. In the context of global demand of energy, especially the conversion energy of transparent semi-conductors oxides to transparent conductive oxides, where play an important role in the development of luminescence materials and solar cells (A. LaRosa, et. al., 2006), (Ravindranadh, K., et al., 2016).

Some thin films oxides, whether doping or composition with semiconductors have high conductivity and high transparency. This materials called transparent conductive oxides, where are the most important semiconductors, which are semiconductor consist of metal united with oxygen such as: In_2O_3, SnO_2, Co_3O_4, etc. which combines two distinctive characters of the most important characters that can be used in the manufacture of electronic devices, these characters are the high conductivity and optical efficiency (Wang LD, et al. (2006).

Many researchers have been interested in thin films that prepared from deposition of SnO_2 due to its usages in many applications such as solar cells, gas sensor, etc. Although used SnO_2 as a photo catalyst to break down a wide range of dyes, phenols, etc., it has low photovoltaic efficiency due to high rate of recombine pairs electron- hole, and this is very important in practice to enhance the performance photo stimulation of SnO_2 (Malik, O., et. al., 2017), (Vidhya, S., et al., 2016).

There are three forms crystalline of cobalt oxides (CoO, Co_2O_3, and Co_3O_4). CoO has a high chemical

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stability but soon oxidizes to Co_3O_4 in the atmosphere, so In recent years there has been a lot of research that studied the Co_3O_4 widely in atmosphere as a promising substance because of its chemical stability. It is a semiconductor material with energy gap lower than (2.5 ev) (Ikhmayies, S.J., et. al., 2008), (Abbas, S., et al., 2014), (Louardi, A., et al., 2016).

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

2. Experimental

:Preparation of tin oxide .2.1

Tin dioxide thin films were synthesized using $SnCl_2.2H_2O$ as a source of tin with 0.2M concentration solution which calculated by the :following equation

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

Hence M is the molar concentration equal to 0.2M, wt. is the weight of$SnCl_2.2H_2O$, M.wtis the molecular weight of$SnCl_2.2H_2O$, V is the volume of deionized water equal to 100 ml.

Then it was dissolved with ethanol 20 ml completely dissolved and then completed the volume to 100 ml with deionized water, and adding a few drops of HCl due to increase the transparency of the solution. Then the solution was mixed and heated to 60°C for 15-20 min to ensure that the .material was fully dissolved

2.2 Preparation of cobalt oxide:

Cobalt oxide thin film was synthesized using $CoCl_2.6H_2O$ (with 0.2M concentration) as a source of cobaltby the same above equation and same synthesis procedure which mentioned in 2.1 .paragraph

2.3 Preparation of composites:

Composites thin films were prepared by mixing the above 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	85	15
Compos 2	50	50

2.4 Deposition set-up:

The main part in the spray process is the atomizer which is 30 cm away from the glass substrate placed on the surface of electrical heater. The glass substrates were heated to 400 °C by an electrical heater. When temperature was reached to 400 °C, The spray process was achieved with a spray time(5 sec), number of sprays (40) and the time which separating between sprays was (1 min). The crystal structure and crystallinity of tin oxide and composites thin films were determined by using a (XRD-6000 Shimadzu) X-ray diffraction diffractometer with Cu-Kα radiation (k =1.5406 A ˚). The absorption spectra of films were recorded using (PC 1650, Shimadzu ultraviolet–visible (UV–Vis) spectrophotometer).

3. Results and Discussion

3.1. Compositional Characterization:

Figures (1-4)illustrate he EDS spectra of tin oxide, cobalt oxide and their composites thin films. Weight and atomic percentages of Co, Sn and O illustrated in table 2, which hint that every oneof composites film contains the components Co, Sn also O.

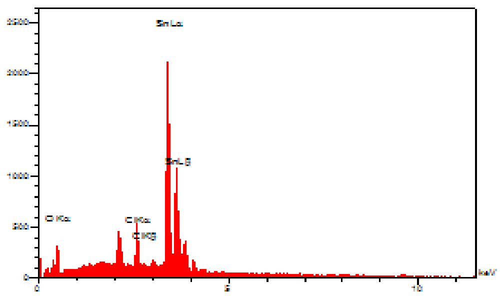

Figure 1: (EDS) spectrum of SnO_2

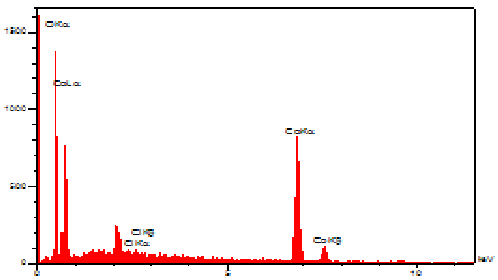

Figure 2: (EDS) spectrum of Co_3O_4

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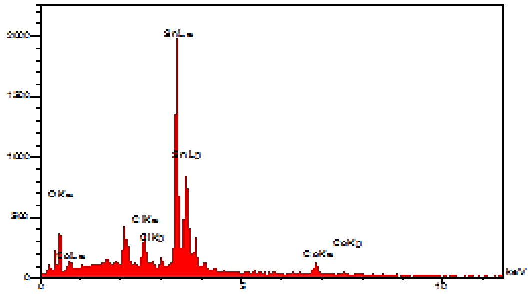

Figure 3: (EDS) spectrum of compos 1

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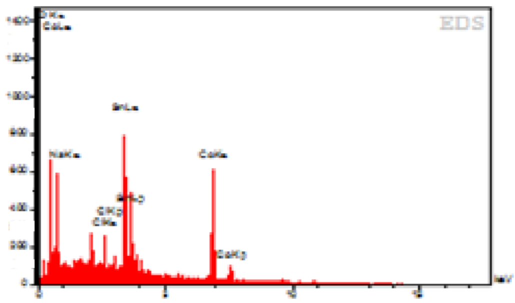


Figure 4: (EDS) spectrum of compos 2

Table 2: Weight and atomic percentages of EDS analysis for SnO_2, Co_3O_4 and their composites

Compound	Element	Weight %	Atomic %
SnO_2	O	33.38	75.11
	Sn	66.62	24.89
Co_3O_4	O	49.16	77.39
	Co	50.84	22.26
Compos 1	O	34.88	77.74
	Co	5.65	4.39
	Sn	59.47	17.86
Compos 2	O	45.21	63.64
	Co	22.32	10.8
	Sn	32.48	24.71

3.2. Structural characterization:

The study of the structural and crystallinity of the prepared thin films were explained by the X-ray diffraction technique. Figures (5-8), shown that peaks correspond to the tetragonal of tin oxide thin film , the cubic of cobalt oxide thin film, and the spinal family of composites thin films. The intensity of the peaks varies with increasing of cobalt ratio, indicating that the crystallization process improves when cobalt is added. Table 3 shows the microstructural constants of films.

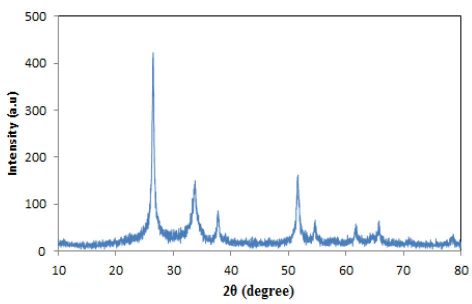
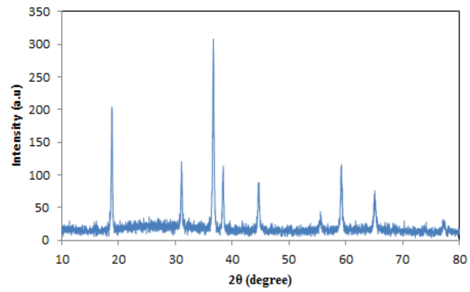


Figure 5:(XRD) diffractogram of SnO_2



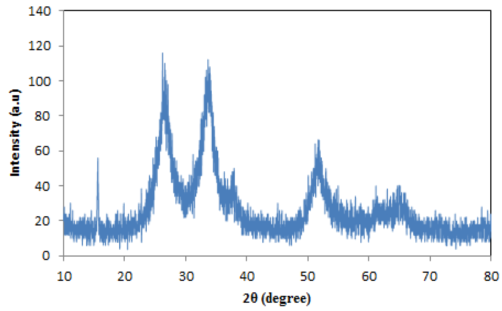


Figure 7: (XRD) diffractogram of compos1

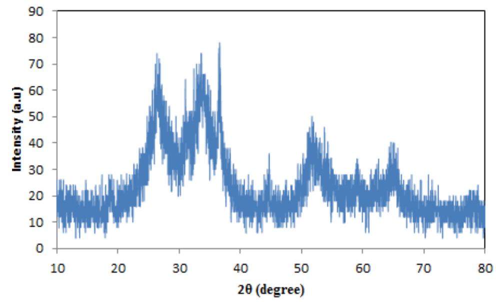


Figure 8: (XRD) diffractogram of compos 2

By using Scherrer'sequation, the average crystalline size of thin films was calculated (Louardi, A., et al. (2016).

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

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 showed in table 3.

Table 4explains that the crystalline size of composites (compos 1, compos 2) decrease with increasing cobalt ratio.

Table 4: Average of crystallite size

Sample	Average of crystallite size (nm)
SnO_2	21.6986
Compos 1	74.0868
Compos 2	63.298
Co_3O_4	57.4384

3.3. Optical characterization:

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3.3.1. Electronic Spectra:

The electronic spectra of tin oxide and composites were elucidated by figures (8-10). The electronic spectra were done by microscopic glass substrate as a reference. It can be known that the absorption decreased with increasing wavelength and increased with increasing cobalt ratio. This Figure 6: (XRD) diffractogram of Co_3O_4 shows that cobalt levels have permeated the self-beams and led to the formation of new prohibited beams (Chowdhury, F.R., et. al., 2011)

Table 3: Microstructural constants of 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
Co_3O_4	18.8888	1 1 1	4.69436	4.6925	34.8158	0.000825	62645.09
	36.7041	3 1 1	2.44652	2.4456	33.42801	0.000895	55448.46
	58.8647	5 1 1	1.56758	1.5670	51.59762	0.000376	203914
Compos 1	26.5533	0 0 3	3.35419	3.3529	4.36349	0.052521	123.3275
	33.6292	2 1 1	2.66286	2.6618	4.562947	0.04803	141.0244
	51.7475	2 1 4	1.76517	1.7645	5.48729	0.033211	245.2629
Compos 2	27.4269	2 0 0	3.2493	3.2480	15.49558	0.004165	5523.079
	43.1318	0 1 4	2.09565	2.0948	96.41887	0.000108	1330589
	47.3695	1 1 4	1.91758	1.9168	189.888	2.77E-05	10163663

3.4. Morphological characterization:

Field emission-scanning electron microscopy technique was used to examine the surface characteristics of tin oxide, cobalt oxide and their composites. The FE-SEM micrographs of films are elucidated in figures (9-12). It has been foundthat the films have bulk compact structures with a homogeneous surface with nanocrystalline crystallites.

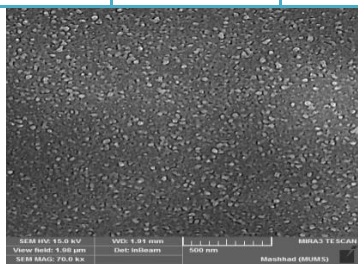

Figure 11: (FE-SEM) image of compos 1

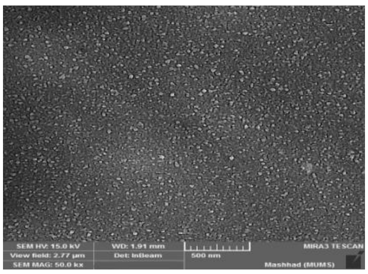

Figure 9: (FE-SEM) image of SnO_2

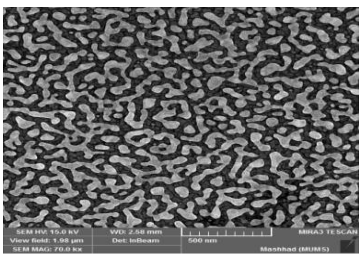

Figure 10: (FE-SEM) image of Co_3O_4

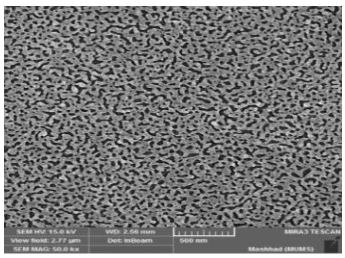

Figure 12: (FE-SEM) image of compos 2

3.5. Optical characterization:

3.5.1. Electronic Spectra:

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Figure (13-16)show the electronic spectra of tin oxide, cobalt oxide and their composites. The electronic spectra were completedthrough glass substrate as a reference. It can be noticed that the absorption decreased with increasing in wavelength and increased with increasing in cobalt ratio.

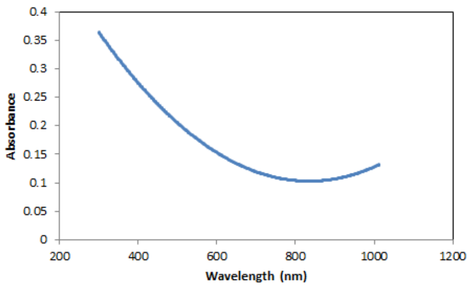

Figure 13: Electronic spectrum of SnO_2

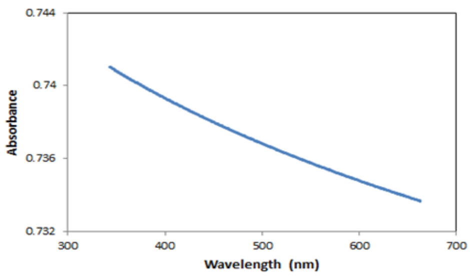

Figure 14: Electronic spectrum of Co_3O_4

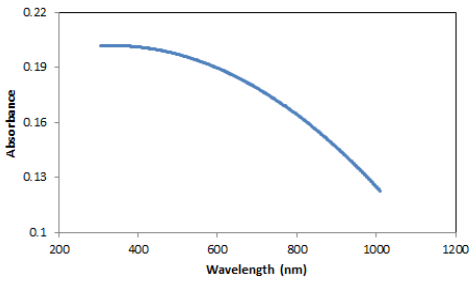

Figure 15: Electronic spectrum of compos 1

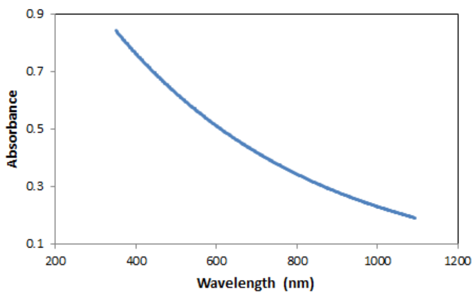

Figure 16: Electronic spectrum of compos 2

3.5.2. Energy gap:

The electronic spectra which described in figures (17-20) were used to extract the optical band gaps of the thin films. The absorption coefficient (α) can be calculated by the following equation (Yousif, S. A. and J. M. Abass, 2013).

$\alpha h\nu = B\,(h\nu - Eg)^n$ ……………..(2)

Where (α) represents the frequency of the light, (B) is 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).

By drawingthe $(\alpha h\nu)^{1/2}$ against (hν), it was found a direct section proving that the transitions must be direct allowed transitions. The energy gap can be estimated by the intercept on energy axis. Table 5 refers to the values of the energy gap for the direct transitions of thin films, with a value of 4.6 eV for the tin oxide. The composites (compos 1, compos 2)are decrease with the increasing of the cobalt ratio this means that the increasing in formation of composites led to the displacement of the absorption edge towards the low energies, where the decreasing in the energy gap indicates the appearance 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.

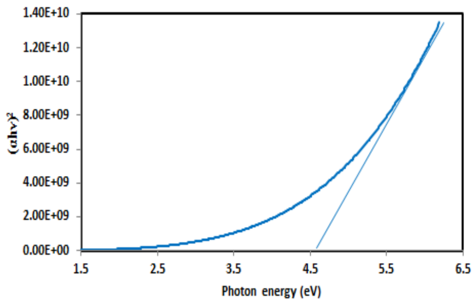

Figure 17: Energy gap of SnO_2

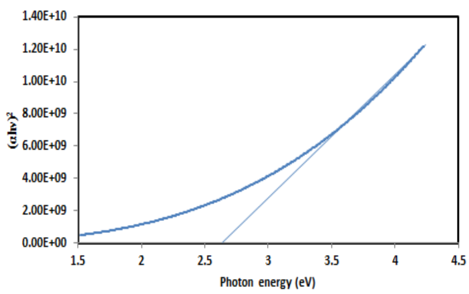

Figure 18: Energy gap of Co_3O_4

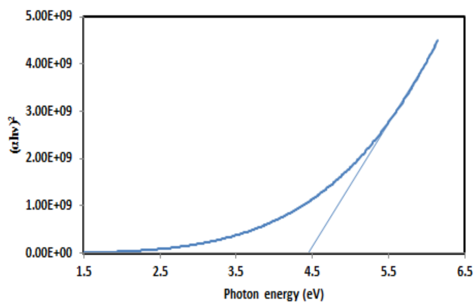

Figure 19: Energy gap of compos 1

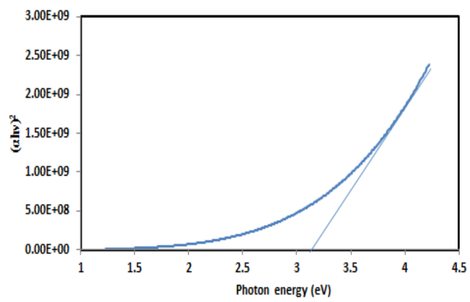

Figure 20: Energy gap of compos 2

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Table 7: Value of energy gaps of thin films

Sample	Eg (eV)
SnO_2	4.5
Compos 1	4.49
Compos 2	3.20
Co_3O_4	2.53

4. Conclusion

Structuralidentification of the prepared thin films wasexplained that all films were polycrystalline and the structure of SnO_2 was tetragonal, the structure of Co_3O_4 was cubic. Using Scherrer equation in XRD analysis, it was found that the average crystallite sizes were decreased by increasing 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 direct type were decreased as cobalt ratio increase.

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