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Study of Optical and Structural Properties of NiO - SnO_2: CdO Nanostructures Thin Films

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Keywords:
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Mixed Nanocomposite.

Abstract

In this research, the preparation of nano thin films of mixed NiO with SnO_2-CdO various concentrations (50،25،75%) was accomplished. The thin films were prepared by chemical spray pyrolysis method and its deposited on glass substrate at a temperature of 200C°. The XRD diffraction displayed the formation of nano composite has a polycrystalline nature. The crystallite size was calculated adopting Scherer's formula. The optical properties explored decreased transmission for the higher concentration of SnO_2-CdO thin films. The energy bandgap values were found with increased concentration of SnO_2-CdO. The AFM analysis shows that the roughness increased with increasing mixing of (2.7nm) to (6.23nm) and average grain size of (13.6nm) to (28.6nm). The SEM shows a fine structure of nanoparticles distributed on the surface average size of nanoparticles (46.5nm).

Introduction

Metal oxide semiconductors are widely used in different sensors [1]. The nano composite is formed by mixing oxides that depend on the concentration of the materials [2-3]. The nano composite is very important for different kinds of applications [4], such as photovoltaic devices ، gas sensors, and solar cells [4-5]. Nickel oxide is one of the p-type semiconductors [6]. CdO is an N-type semiconductor (whose direct band gap) is (2.2ev) [7]. It is high electrical conductivity and low electrical resistance, [7-9]. SnO_2 is an N- type semiconductor which is applicably widely used in electronics. Solar cells and gas sensors [10-11], nano campsites and Optimum properties, that are significantly superior to the single oxide, nano composite improve the properties in electrical and electronic applications, where the physical properties of nano composites are mainly affected by the nano size and chemical composition of the material used in the applications [12-13]. Commonly used oxides are tin oxide, nickel oxide, cadmium dioxide, iron oxide, and tungsten oxide. These materials have successfully been employed to detect a range of gas vapours, particularly ethanol, methanol, ammonia, and hydrogen sulphide [14]. Thick film technology, which is often used to fabricate sensors, possesses many advantages, such as low cost, simple construction,

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small size and good sensing properties [15-16]. In addition, this approach provides reproducible films that consist of a well-defined microstructure with grains and grain boundaries that can be studied easily [17].

In this work, we have prepared NiO-SnO2: CdO nano composites thin films by chemical spray pyrolysis method. The goal of this work is to synthesize NiO-SnO_2: CdO -nanocomposites with different ratios. The effect of different ratios on the film properties, like crystal structure, surface morphology, and optical transmittance were studied and the obtained results were compared and discussed .

Experimental details

NiO-SnO_2: CdO nano thin films were grown on glass substrate by a chemical spray method. The glass substrate was cleaned by deionized water and mixed with alcohol to prepare the precursor solutions. The stoichiometric amounts of ($Nicl_2.H_2O$ 99 % purity), ($SnCl_2.2H_2O$ 99% purity), and ($CdCl_2.H_2O$ purity 98.8 %) have dissolved (2.37gm) of $Nicl_2$ and (1.47gm) of $sncl_2$ and (1.83gm) of $cdcl_2$ in water. NiO was mixed with SnO2: CdO and the solution was stirred for 60 minutes at 50°C using (0.1M) aqueous solutions. Firstly, NiO un doped solution, after that NiO mixed with SnO_2: CdO values were 25%ml and 50%ml,75%ml and spared on substrate. The spraying time period was 5s followed by 30s wait intervals and average deposition 2ml/min, and substrate temperature 200C° during spraying. Structural characteristics were examined by XRD (Shimadzu 6000PW 1050 A˚ Target: Cu-kα, Scan mode: continuous scan, Current: 30 mA, Voltage: 40 kV, Wavelength 1.5406 A). AFM (AA3000) is used to identify the film topography. The optical transmission and optical absorption were measured using uv-vis spectrophotometer type (sp-8001) in the wavelength range 300-1100nm.

Results and discussion

1. X-Ray diffraction

Figure 1 depicts the XRD patterns of NiO-SnO2: CdO Nano composites on glass. The structure is polycrystalline, as can be seen in this figure. In order to calculate the size of crystals, we used Scherer's formula $D = \frac{K\lambda}{\beta \cos \theta}$ [19].

NiO has an average crystallite size of (18.6 nm), which agrees with Vigneshumar [20]. There are several peaks in this structure. The mixed films at ratio 25 percent NiO-75 percent SnO2: CdO figure (1-b), the average G.S increased to (22.5nm). Figure (1-c) explains decreased peaks of NiO 50 percent with mixing50 percent CdO:SnO2 (c) and orient at (Hexagonal structure) and card No (1302-035-00),average Grain Size (35.58nm), 75 percent NiO-25 percent Sn (36.59nm).

2. Atomic force microscope

Figure (2) shows atomic force microscopy to study the surface structure of thin films. AFM images of NiO and CdO: SnO_2 films are shown in figures (2-a, b, C, d) which have a “high homogeneous and regular granular distribution”, the grain size of (a) are (13.6nm) and the average roughness (R.M.S) was (2.34nm). Figure (2-b) shows the average grain size (18.6nm), the (R.M.S) which was (5.21nm), and the average roughness (4.20 nm). Figure (2-c) shows (c), the average grain size (19.3nm), R.M.S (6.33nm), and the average roughness (5.51nm). Figure (d) shows the average grain size (28.6nm), the average roughness which was (6.23nm), and the R.M.S (7.74nm). The average grain size increased with the increased mixed SnO_2: CdO.

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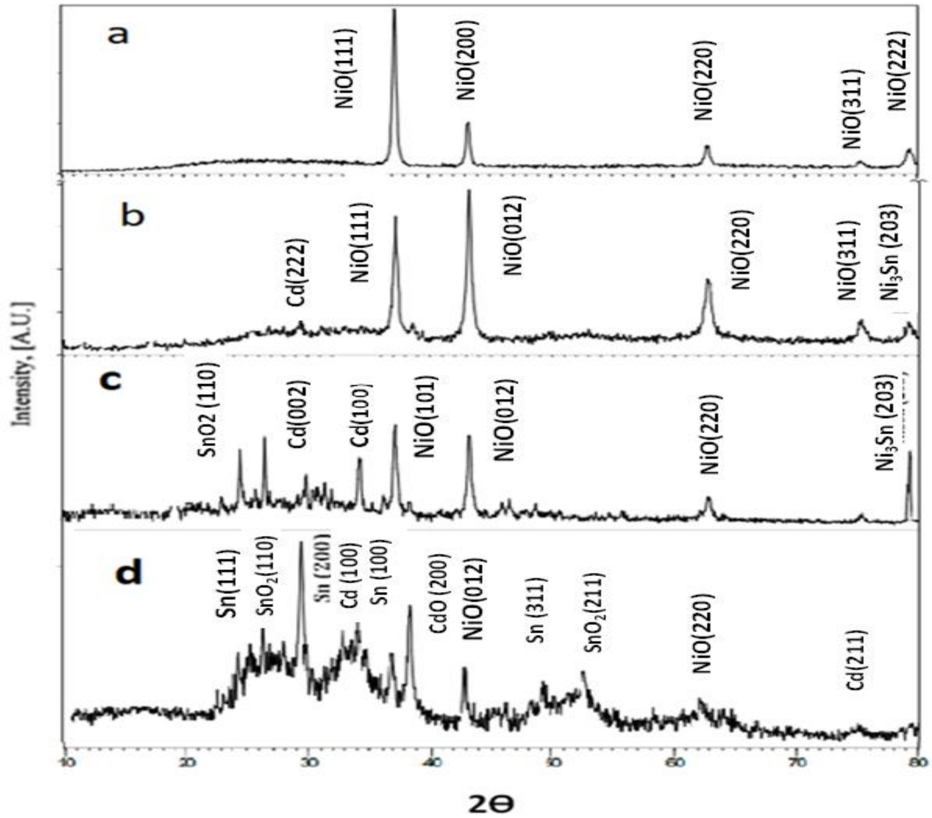
Figure. 1. XRD spectra of the (a) NiO undoped, (b) 25%, (c) 50% and (d) 75% Adopted CdO:SnO2



3. Scanning electron microscopy

Figure (3-3) shows SEM images Of films (c) on glass substrate. The images show the structure of nanoparticles randomly distribution and give information about the nanostructures of the surface [19], and the average grain size that varies from (41.08nm) to (54.20nm). This structure increases the surface area and improves the properties in many applications.

sample	2Θ Deg	FWHM Deg	d_{hkl} Exp.(Å)	G.S (nm)	phase	hkl
a	19.15	0.2952	2.41547	25.49	NiO	111
	26.49	0.2952	2.0943	25. 1	NiO	200
	31.39	0.3444	1.47905	19.67	NiO	220
	34.26	0.601	1.6213	10.47	NiO	311
	37.09	0.492	1.20564	12.41	NiO	222
b	19.32	0.1476	2.84926	51.79	Cd	002
	26.61	0.246	2.41921	30.59	NiO	101
	31.83	0.246	2.09375	30.01	NiO	012
	34.74	0.492	1.47952	13.774	NiO	220
	37.24	0.3936	1.26259	15.97	NiO	311
	43.28	0.48	1.20734	12.73	Ni_3Sn	203
	26.49	0.1476	3.36429	53.80	SnO_2	110

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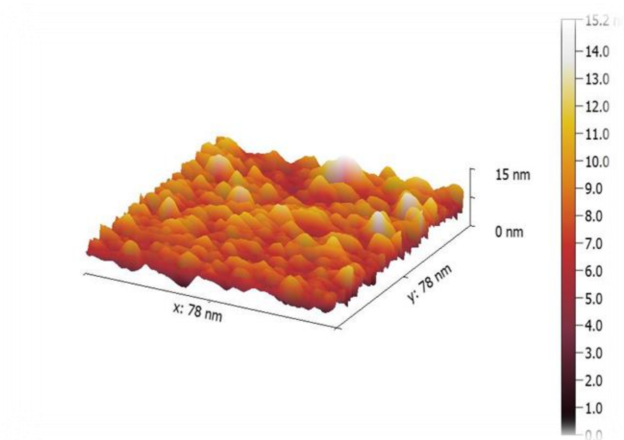
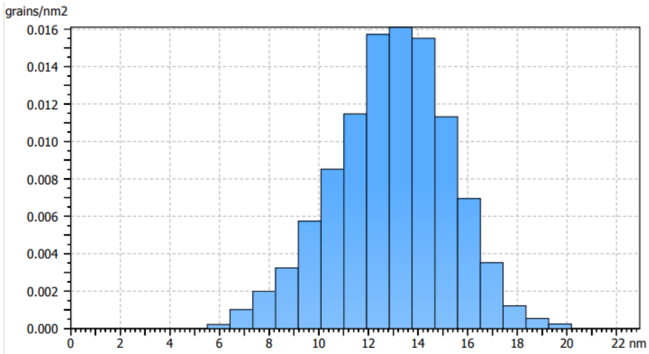
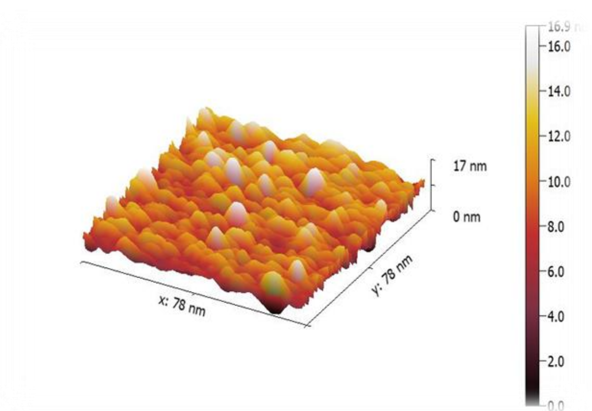
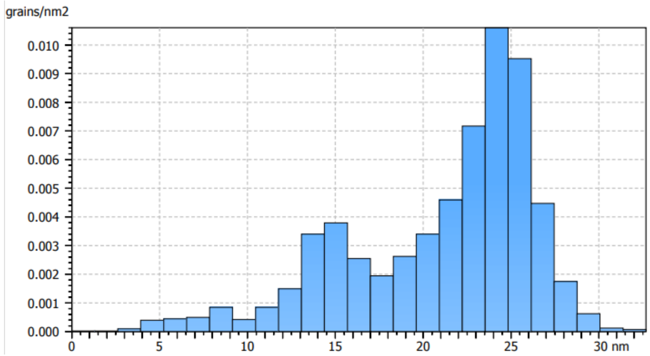
c	31.39	0.1476	2.84926	53.80	Cd	002
	34.26	0.2952	2.61703	26.90	Cd	100
	37.09	0.246	2.42384	32.28	NiO	101
	43.22	0.246	2.09291	32.28	NiO	012
	62.73	0.36	1.47989	22.05	NiO	220
	19.15	0.1968	4.63425	40.35	Ni_3Sn	203
d	23.51	0.3936	3.874	19.752	Sn	111
	26.47	0.1968	3.32623	39.27	SnO_2	110
	30.41	0.1968	2.93936	38.93	Sn	200
	34.10	0.7872	2.62884	9.64	Cd	100
	34.91	0.1968	2.56975	38.49	Sn	100
	38.59	0.3444	2.33279	21.76	CdO	200
	43.31	0.2952	2.8894	25.002	NiO	102
	46.51	0.1968	1.95252	37.073	Sn	311
	51.65	0.2952	1.76944	24.21	SnO_2	211
	62.82	0.3444	1.47917	19.67	NiO	110
	75.58	0.2952	2.8894	18.22	Cd	211

Table 1 XRD peaks parameters for NiO-CdO: SnO_2 thin films prepared different mixed









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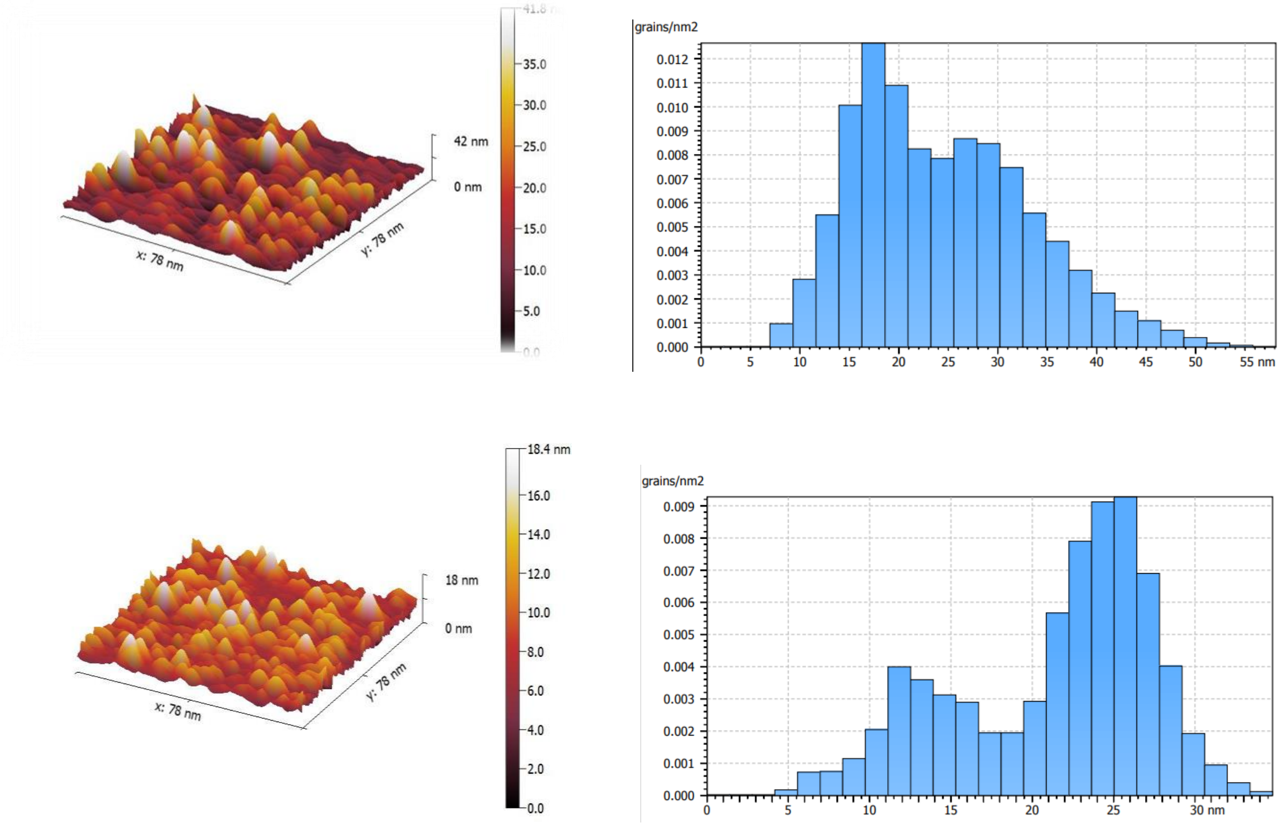

Figure (2) AFM image (for 25% NiO pure and mixed with cadmium tin oxide different mixed.

4. Optical properties

The optical properties are importance as thin films and they are used as a gas sensor. These properties include transmittance and energy gap.

- **Transmittance**

Figure (4) shows pure NiO which is mixed with SnO_2: CdO thin films. According to figure (4), the value of pure NiO transmission at 750nm wave length is 71%, and when mixed with thin films it decreases with the increasing ratio of SnO_2: CdO. This is due to the effect of SnO_2: CdO oxide, which leads to an increase in the density of oxygen vacancies, as it affects the crystal structure of the films and causes a change in the nature of surfaces, in addition to increasing the surface roughness of the films, as shown in the images of the atomic force microscopy as the surface roughness increases the optical scattering and reduces the transmittance; this behavior agrees with the Chakraborty [20].

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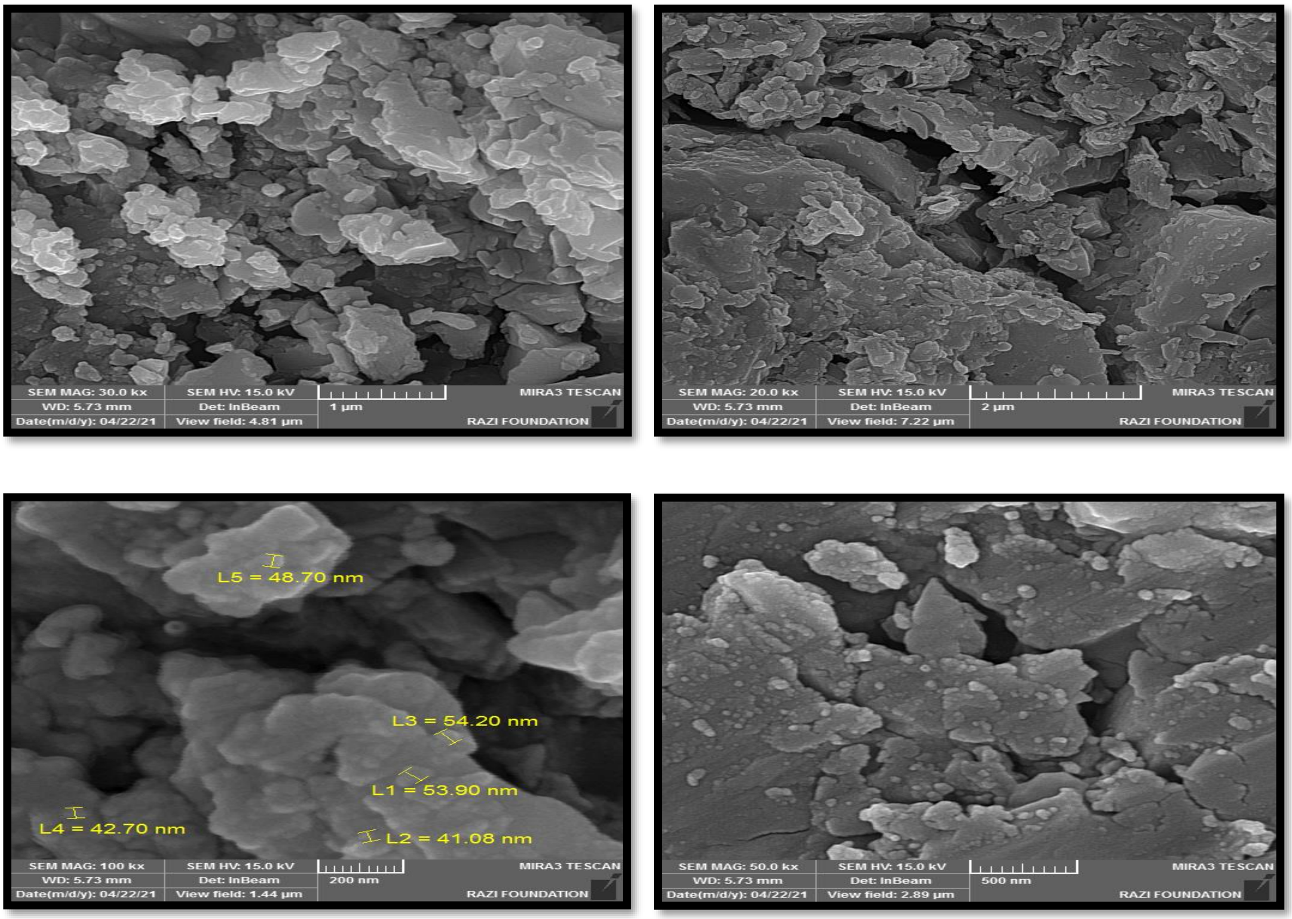

Figure (3) SEM images of NiO 50% with 50% CdO:SnO2

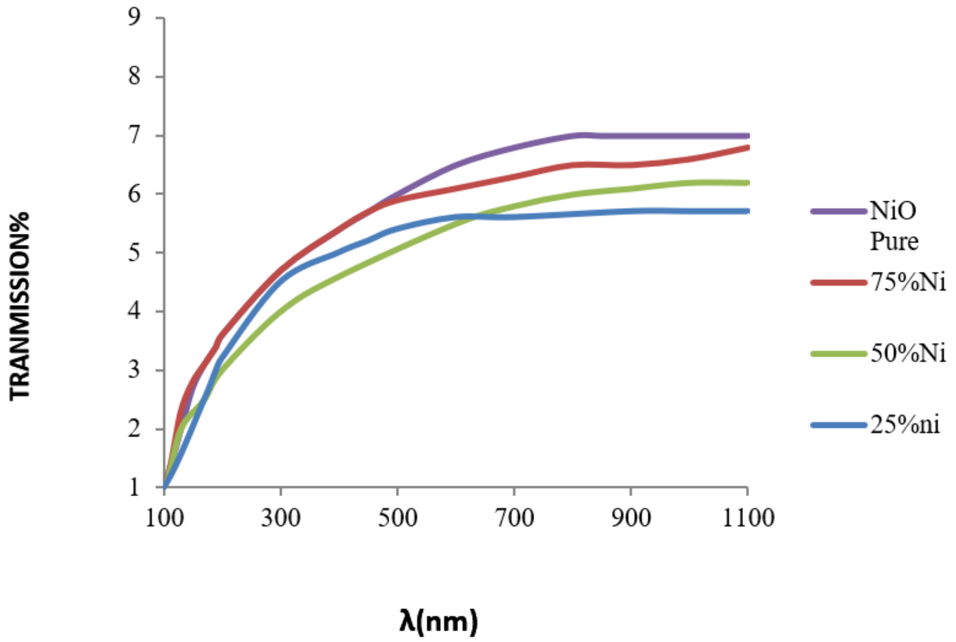

Figure 4. Optical transmission for NiO pure and mixed(SnO_2:CdO) of thin films.

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Table 2 shows the values of transmittance for NiO-CdO:SnO_2 thin films

Sample	Transmission%
A	80%
B	68%
C	60%
D	55%

- **Energy gap**

The optical energy gap is of a great importance for determining the possibility of using thin films in the application of sensors, as it gives a clear idea of the optical absorption, as the film is transparent to radiation whose energy is less than the energy gap Eg> hυ) and as the absorbing radiation whose energy is greater than it ($h\upsilon \leq Eg$). The value of the energy gap in the allowed direct electronic transitions of the NiO- SnO_2: CdO films has been calculated by drawing the graphic relationship between $(\alpha h\upsilon)^2$ and the energy of the photon, therefore we get the value of the energy gap for the allowed direct transition. Figure (4-9) shows the permissible direct energy gap of the films NiO (2.1 ev), It was discovered that increasing the mixing ratio increased the value of the energy gap due to the filling of the lower levels of the conduction beam with electrons. So it requires high energy to irritate the electron from the valence band to conduction band, which leads to a high optical energy gap known as the effect of Burstein - alga (transformation). This effect causes absorption to be shifted toward higher energies when the mixing ratio and impurity proportion are understood in a way that agrees with the Sophie [21].

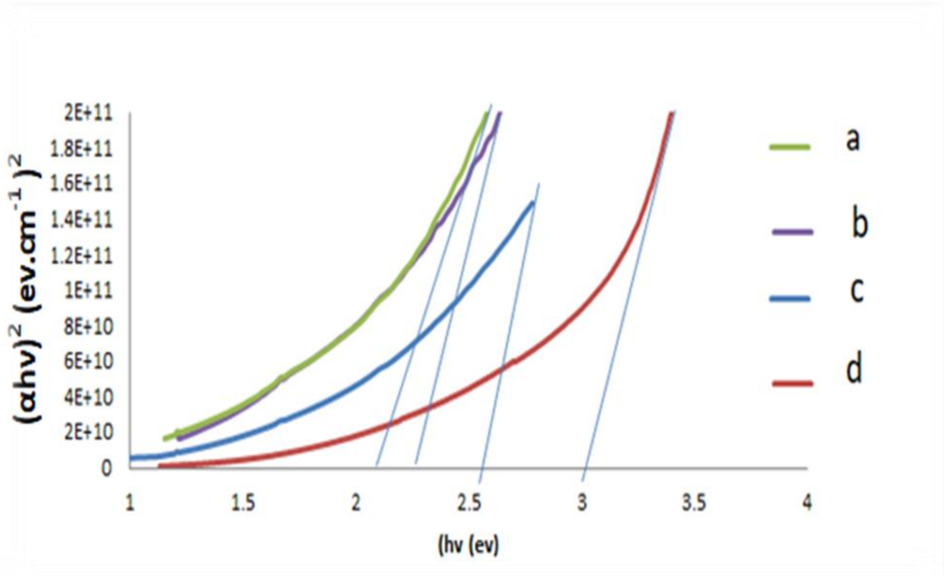

Figure 4. Optical energy gap of NiO pure and mixed SnO_2: CdO of thin films (a:NiO Pure, b:NiO75%, C: NiO50%, d:NiO25%)

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Conclusion

Nano structure NiO- SnO_2: CdO films deposited on glass and study the effect of the quantity of solution of SnO_2: CdO and NiO on the structural properties. Nanostructures were obtained, as the atomic force microscopy and scanning electron microscopy showed the average of particle size **(41.08nm)**. The surface roughness increased with increasing mixing from (2.34nm) to (6.23nm). Increasing the surface roughness leads to an increase in the reaction of the gas with the surface and increases sensitivity. Optical analysis of nano composites is achieved by using UV-Vis absorption spectra ranging from 350 to 1100 nm. Gap energy increased 2.1ev volts to 3ev volts with increasing 75% concentration of SnO_2: CdO nan composites.

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