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Role of ZnO content on the structural, morphology and optical properties of $(NiO)_{1-x}$ $(ZnO)_x$ thin films prepared by pulsed laser deposition technique

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Abstract. $(NiO)_{1-x}$ $(ZnO)_x$ compounds were prepared with different composition ratios. The compounds were obtained by mixing Nickle oxide and zinc oxide in the appropriate ratio and sintered at 1000°C for six hours. Pulsed laser deposition (PLD) method which is simple and inexpensive method was used to deposit $(NiO)_{1-x}$ $(ZnO)_x$ thin films on glass substrate at ambient temperature. Structural, optical and properties were investigated. The structures investigation obtained from x-ray diffraction showed that the prepared of compound as well as thin films have polycrystalline structure where the diffraction peaks were identical with the cubic NiO and hexagonal ZnO for x=0 and 1.0 while the structure of the residual x values was identical with the both phases. The average values of the crystallite size increases from 29.3 nm to 32.4 nm when x increases from 0 to 1.0. Thickness interferometry measurement showed that thickness of the prepared thin films was ≈150 nm. The optical absorbance and transmittance spectrum provided from UV-spectrophotometer were used to estimate the optical parameters like optical energy gap Eg, refractive index, extinction coefficient and real and imaginary dielectric constants. The data showed that the optical energy gap as well as the optical constants decreases with the increasing of ZnO content in the prepared thin films.

Keywords. Nickel oxide thin films, zinc oxide thin films pulsed laser deposition (PLD) technique, optical properties.

1. Introduction

Zinc Oxide N-type semiconductor compound has a (3.4eV) energy gap and a (60 MV) binding capacity [1, 2]. It is considered one of the most prevalent semiconductors and is widely used in industrial and academic research due to its unique characteristics [3, 4]. Nontoxic, white color, chemically and thermally stable, available in nature, low price and eco-friendly, has a hexagonal structure [5]. Because of these important properties, zinc oxide is an important substance in applications such as optoelectronic, blue and ultraviolet optical devices, varistors, solar cell, surface acoustic wave devices, gas sensor, heat mirror for energy saving, photodetectors, transparent conducting films, nanolasers, biomaterials, laser diodes, biomedical application, window material for display, cosmetics, light emitting diodes, sunscreens and spintronics [6, 7, 8]. In order to increase applications it was mixed with a nickel oxide compound, a black metal base compound of p-type [9, 10]. PLD was used to prepare thin films of two compounds mixed with zinc oxide and nickel oxide in different proportions.

2. Experimental

Zinc oxide and nickel oxide were obtained with suitable amount of high purity (99.99%) and the compound $(NiO)_{1-x} (ZnO)_x$ was formed as x= (0.0, 0.2, 0.4, 0.6, 0.8, and 1) which were weighed using electronic balance with the lowest number of grams. The material, in quartz ampoules (length 25 cm and inner diameter 6 mm), was heated to 1000 ° C for 6 hours. The oven temperature was raised at a rate of 10 ° C / min. It was pressed into a disc with a diameter (1 cm) and a thickness (0.5 cm), using a hydraulic piston type (SPECAC), under pressure of 7 tons at a time of 15 seconds. The thin films were made by PLD techneque. Pulsed laser deposition was used inside a vacuum chamber at a pressure ($2 * 10^{-3}$ Toor), the laser beam passes through the incident window on the target surface at an angle of 45 degrees. The substrate is placed in front of the target with its surface parallel to the target. An adequate gap between the target and the substrate has been maintained so that the substrate holder does not hinder the incident laser beam. The distance between the target and the substrate is 2 cm, while the distance between the target and the laser source is 10 cm. PLD technology was used to make thin membranes on substrates inside a 500 mJ and 400 pulse discharge chamber at 6 Hz.

3. *Results and discussion*

3.1. XRD Analysis

The structural characteristics of the $(NiO)_{1-x} (ZnO)_x$ compound were conducted to determine the crystalline phase and the degree of crystallization and possible modifications due to the difference of oxides. Figure 1 and Table 1 show the type of XDR analysis of $(NiO)_{1-x} (ZnO)_x$ compound of six specific ratios of the powder, whereas (2θ=37.24, 43.26, 62.85, 75.40, 79.35) degree of nickel oxide and (hkl=111, 200, 220, 311, 222) respectively appeared in all percentages except the individual zinc oxide ratio. The zinc oxide (2θ=31.83, 34.50, 36.33, 47.63, 56, 66, 62.69, 66.47, 67.99, 69.14, 72.66, 76.98) degree and (hkl=100, 200,101, 102, 110, 103,200, 112, 201, 004, 202) respectively appeared in all percentages except the individual nickel ratio. The XRD analysis of thin films shown in Figure 2 and Table 2 declared the nickel oxide compound in only three percentages, 0, 0.2 and 0.4. The zinc oxide appeared in all x values except at x=0 for nickel oxide. This results is similar to the findings of [11, 12].

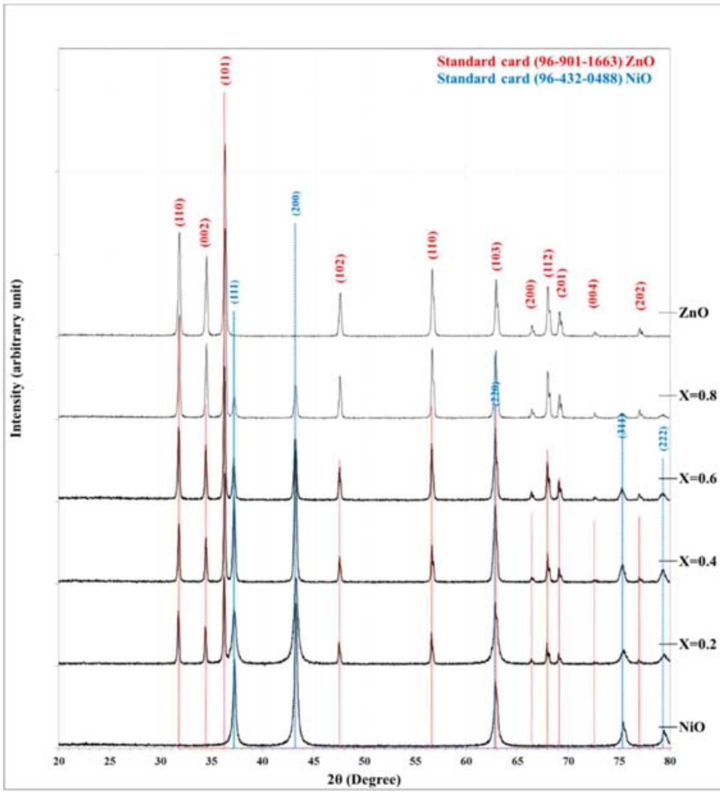

Figure 1. (XRD) of the $(NiO)_{1-x}(ZnO)_x$ powder.

Table 1. Analysis of (XRD) of the $(NiO)_{1-x}(ZnO)_x$ powder.

	2θ (Deg.)	**FWHM (Deg.)**	**dhkl Exp. (Å)**	**G.S (nm)**	**dhkl Std. (Å)**	**Phase**	**hkl**	**card No.**
NiO	37.2492	0.3383	2.4120	24.8	2.4148	Cub. NiO	(111)	96-432-0488
	43.2694	0.3721	2.0893	23.0	2.0913	Cub. NiO	(200)	96-432-0488
	62.8523	0.5073	1.4774	18.4	1.4788	Cub. NiO	(220)	96-432-0488
	75.4002	0.5411	1.2596	18.6	1.2611	Cub. NiO	(311)	96-432-0488
	79.3574	0.4059	1.2065	25.4	1.2074	Cub. NiO	(222)	96-432-0488
0.2	31.7362	0.2706	2.8172	30.5	2.8137	Hex.ZnO	(100)	96-901-1663
	34.4081	0.2706	2.6043	30.7	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2345	0.2706	2.4771	30.9	2.4754	Hex.ZnO	(101)	96-901-1663
	37.2153	0.4059	2.4141	20.7	2.4148	Cub. NiO	(111)	96-432-0488
	43.2694	0.5411	2.0893	15.8	2.0913	Cub. NiO	(200)	96-432-0488
	47.4972	0.2706	1.9127	32.1	1.9110	Hex.ZnO	(102)	96-901-1663
	56.5614	0.3382	1.6258	26.7	1.6245	Hex.ZnO	(110)	96-901-1663
	62.8523	0.4397	1.4774	21.2	1.4788	Cub. NiO	(220)	96-432-0488
	67.9256	0.3382	1.3788	28.3	1.3782	Hex.ZnO	(112)	96-901-1663
	69.0417	0.2367	1.3593	40.7	1.3582	Hex.ZnO	(201)	96-901-1663

	75.4002	0.6426	1.2596	15.6	1.2611	Cub. NiO	(311)	96-432-0488
	79.3912	0.7440	1.2060	13.9	1.2074	Cub. NiO	(222)	96-432-0488
	31.8038	0.3044	2.8114	27.1	2.8137	Hex.ZnO	(100)	96-901-1663
	34.4419	0.2367	2.6019	35.1	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2683	0.2367	2.4749	35.3	2.4754	Hex.ZnO	(101)	96-901-1663
	37.2153	0.3044	2.4141	27.5	2.4148	Cub. NiO	(111)	96-432-0488
	43.2356	0.3720	2.0909	23.0	2.0913	Cub. NiO	(200)	96-432-0488
0.4	47.5310	0.2705	1.9114	32.1	1.9110	Hex.ZnO	(102)	96-901-1663
	56.5953	0.3044	1.6249	29.6	1.6245	Hex.ZnO	(110)	96-901-1663
	62.8523	0.4735	1.4774	19.7	1.4788	Cub. NiO	(220)	96-432-0488
	66.4036	0.2368	1.4067	40.1	1.4069	Hex.ZnO	(200)	96-901-1663
	67.9594	0.2368	1.3782	40.5	1.3782	Hex.ZnO	(112)	96-901-1663
	69.0755	0.2367	1.3587	40.7	1.3582	Hex.ZnO	(201)	96-901-1663
	75.3326	0.5073	1.2606	19.8	1.2611	Cub. NiO	(311)	96-432-0488
	79.3236	0.5412	1.2069	19.1	1.2074	Cub. NiO	(222)	96-432-0488
	31.7700	0.2706	2.8143	30.5	2.8137	Hex.ZnO	(100)	96-901-1663
	34.4419	0.2705	2.6019	30.7	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2683	0.2367	2.4749	35.3	2.4754	Hex.ZnO	(101)	96-901-1663
	37.1815	0.3382	2.4162	24.8	2.4148	Cub. NiO	(111)	96-432-0488
	43.2356	0.3382	2.0909	25.3	2.0913	Cub. NiO	(200)	96-432-0488
0.6	47.5648	0.3044	1.9102	28.5	1.9110	Hex.ZnO	(102)	96-901-1663
	56.5953	0.3044	1.6249	29.6	1.6245	Hex.ZnO	(110)	96-901-1663
	62.8523	0.4397	1.4774	21.2	1.4788	Cub. NiO	(220)	96-432-0488
	66.3698	0.2706	1.4073	35.1	1.4069	Hex.ZnO	(200)	96-901-1663
	67.9256	0.3044	1.3788	31.5	1.3782	Hex.ZnO	(112)	96-901-1663
	69.0755	0.2706	1.3587	35.6	1.3582	Hex.ZnO	(201)	96-901-1663
	75.3326	0.5073	1.2606	19.8	1.2611	Cub. NiO	(311)	96-432-0488
	76.9222	0.2029	1.2385	50.0	1.2377	Hex.ZnO	(202)	96-901-1663
	79.2221	0.5412	1.2082	19.1	1.2074	Cub. NiO	(222)	96-432-0488
	31.8377	0.2367	2.8085	34.9	2.8137	Hex.ZnO	(100)	96-901-1663
	34.4758	0.2367	2.5994	35.1	2.6035	Hex.ZnO	(002)	96-901-1663
	36.3021	0.2367	2.4727	35.3	2.4754	Hex.ZnO	(101)	96-901-1663
	37.2492	0.3044	2.4120	27.5	2.4148	Cub. NiO	(111)	96-432-0488
	43.2356	0.3044	2.0909	28.1	2.0913	Cub. NiO	(200)	96-432-0488
	47.5986	0.3382	1.9089	25.7	1.9110	Hex.ZnO	(102)	96-901-1663
0.8	56.6291	0.2706	1.6240	33.3	1.6245	Hex.ZnO	(110)	96-901-1663
	62.8861	0.3383	1.4767	27.5	1.4788	Cub. NiO	(220)	96-432-0488
	66.4036	0.2706	1.4067	35.1	1.4069	Hex.ZnO	(200)	96-901-1663
	67.9932	0.3382	1.3776	28.3	1.3782	Hex.ZnO	(112)	96-901-1663

	69.1094	0.3044	1.3581	31.7	1.3582	Hex.ZnO	(201)	96-901-1663
	72.5930	0.2029	1.3013	48.6	1.3017	Hex.ZnO	(004)	96-901-1663
	75.2988	0.4735	1.2611	21.2	1.2611	Cub. NiO	(311)	96-432-0488
	76.9899	0.2029	1.2375	50.0	1.2377	Hex.ZnO	(202)	96-901-1663
	79.3236	0.5411	1.2069	19.1	1.2074	Cub. NiO	(222)	96-432-0488
	31.8377	0.2368	2.8085	34.9	2.8137	Hex.ZnO	(100)	96-901-1663
	34.5096	0.2367	2.5969	35.1	2.6035	Hex.ZnO	(002)	96-901-1663
	36.3360	0.1691	2.4705	49.4	2.4754	Hex.ZnO	(101)	96-901-1663
	47.6325	0.3044	1.9076	28.5	1.9110	Hex.ZnO	(102)	96-901-1663
ZnO	56.6629	0.2706	1.6231	33.4	1.6245	Hex.ZnO	(110)	96-901-1663
	62.9200	0.2367	1.4759	39.3	1.4772	Hex.ZnO	(103)	96-901-1663
	66.4713	0.2367	1.4054	40.1	1.4069	Hex.ZnO	(200)	96-901-1663
	67.9932	0.3382	1.3776	28.3	1.3782	Hex.ZnO	(112)	96-901-1663
	69.1432	0.3044	1.3575	31.7	1.3582	Hex.ZnO	(201)	96-901-1663
	72.6607	0.2706	1.3002	36.4	1.3017	Hex.ZnO	(004)	96-901-1663
	76.9899	0.2029	1.2375	50.0	1.2377	Hex.ZnO	(202)	96-901-1663

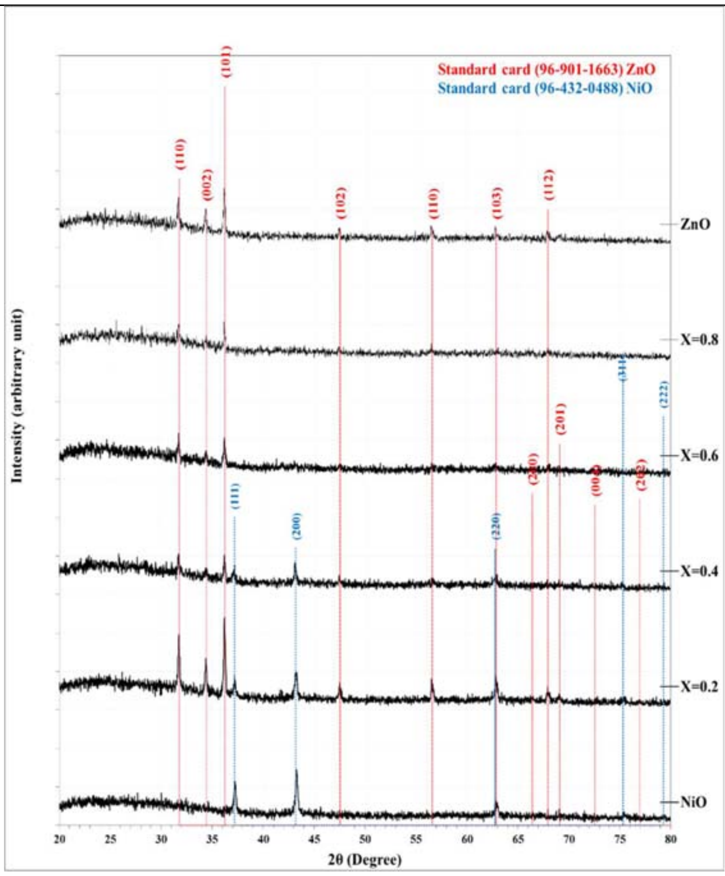

Figure 2. Analysis (XRD) of compound (NiO) $_{1-x}$ (ZnO) $_x$ thin films prepared by PLD technique.

Table 2. Analysis (XRD) of compound $(NiO)_{1-x}(ZnO)_x$ thin films prepared by PLD technique.

	2θ (Deg.)	**FWHM (Deg.)**	**d_{hkl} Exp.(Å)**	**G.S (nm)**	**d_{hkl} Std.(Å)**	**Phase**	**hkl**	**card No.**
	37.2834	0.2995	2.4098	28.0	2.4148	Cub. NiO	(111)	96-432-0488
NiO	43.2727	0.2567	2.0892	33.3	2.0913	Cub. NiO	(200)	96-432-0488
	62.9519	0.3423	1.4753	27.2	1.4788	Cub. NiO	(220)	96-432-0488
	31.7647	0.2139	2.8148	38.6	2.8137	Hex.ZnO	(100)	96-901-1663
	34.3743	0.2567	2.6068	32.4	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2567	0.2139	2.4757	39.1	2.4754	Hex.ZnO	(101)	96-901-1663
	37.2406	0.2567	2.4125	32.7	2.4148	Cub. NiO	(111)	96-432-0488
	43.2299	0.2995	2.0911	28.5	2.0913	Cub. NiO	(200)	96-432-0488
0.2	47.5080	0.2139	1.9123	40.6	1.9110	Hex.ZnO	(102)	96-901-1663
	56.5348	0.2567	1.6265	35.1	1.6245	Hex.ZnO	(110)	96-901-1663
	62.7807	0.3422	1.4789	27.2	1.4788	Cub. NiO	(220)	96-432-0488
	67.9144	0.2567	1.3790	37.3	1.3782	Hex.ZnO	(112)	96-901-1663
	69.0267	0.2995	1.3595	32.2	1.3582	Hex.ZnO	(201)	96-901-1663
	31.7219	0.2139	2.8185	38.6	2.8137	Hex.ZnO	(100)	96-901-1663
	34.4171	0.2995	2.6037	27.8	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2139	0.2567	2.4785	32.6	2.4754	Hex.ZnO	(101)	96-901-1663
0.4	37.1979	0.2139	2.4152	39.2	2.4148	Cub. NiO	(111)	96-432-0488
	43.1016	0.2995	2.0970	28.5	2.0913	Cub. NiO	(200)	96-432-0488
	47.4652	0.2994	1.9139	29.0	1.9110	Hex.ZnO	(102)	96-901-1663
	56.5348	0.2995	1.6265	30.1	1.6245	Hex.ZnO	(110)	96-901-1663
	62.7380	0.3423	1.4798	27.2	1.4788	Cub. NiO	(220)	96-432-0488
	31.7219	0.2567	2.8185	32.2	2.8137	Hex.ZnO	(100)	96-901-1663
0.6	34.4171	0.2994	2.6037	27.8	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2139	0.2566	2.4785	32.6	2.4754	Hex.ZnO	(101)	96-901-1663
	31.7647	0.1711	2.8148	48.3	2.8137	Hex.ZnO	(100)	96-901-1663
0.8	34.4171	0.2994	2.6037	27.8	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2139	0.2139	2.4785	39.1	2.4754	Hex.ZnO	(101)	96-901-1663
	31.6791	0.2567	2.8222	32.2	2.8137	Hex.ZnO	(100)	96-901-1663
	34.3743	0.2567	2.6068	32.4	2.6035	Hex.ZnO	(002)	96-901-1663
	36.2139	0.2566	2.4785	32.6	2.4754	Hex.ZnO	(101)	96-901-1663
ZnO	47.4652	0.2995	1.9139	29.0	1.9110	Hex.ZnO	(102)	96-901-1663
	56.4920	0.3422	1.6277	26.4	1.6245	Hex.ZnO	(110)	96-901-1663
	62.7807	0.1711	1.4789	54.4	1.4772	Hex.ZnO	(103)	96-901-1663

67.8717	0.2995	1.3798	32.0	1.3782	Hex.ZnO	(112)	96-901-1663

3.2. Optical analysis

Figure 3 illustrates the optical transmittance curves as a function of the wavelength of $(NiO)_{1-x}(ZnO)_x$ thin films for six specific ratios deposited on glass substrates using pulsed laser deposition technique. It is clear that the the lowest transparency attain for $(NiO)_{0.8}(ZnO)_{0.2}$ for x=0.2 while more transparent(lowest absorption) thin film was (ZnO) where x=1.0, this indicates more good opacity and transparency of the prepared thin film respectively.

It is clear that the absorption edge show shift to lower energies (IR) or to higher energies (UV) with the addition of zinc oxide to the host material (NiO). Moreover there is IR shift take place at x=0.2, 0.4 and 1.0while there are UV in $(NiO)_{1-x}(ZnO)_x$ thin films at x= 0.6 and 0.8.The absorption edge is shifted to lower or higher energies related to the increase and decrease of crystallite size. The average crystallite size corresponding to the main peaks appear in the diffraction pattern get to increase but in non-systematic manner with the increase of x value, indeed the crystallite size changes from 29.5, 34.26, 33.34, 30.86, 38.4, 32.4nm when x increases from 0 to 1.0. Figure 4 show the variation of $(\alpha h\nu)^2$ with $(h\nu)$ *for* $(NiO)_{1-x}(ZnO)_x$ *thin films* prepared by PLD technique. It is obvious the transition is allowed direct where r= 0.5. The estimated value of optical energy gaps were illustrated in table 3. The red and blue shifts of the energy gap related to the increase and or reduction of crystallite size respectively. Figures (5, 6, 7, 8) showed the plot diagrams of (n,k, ε_1,ε_2)of $(NiO)_{1-x}(ZnO)_x$ thin films of six proportions. The results of optical characteristics are presented in Table 3. This is coincided with the results [13].

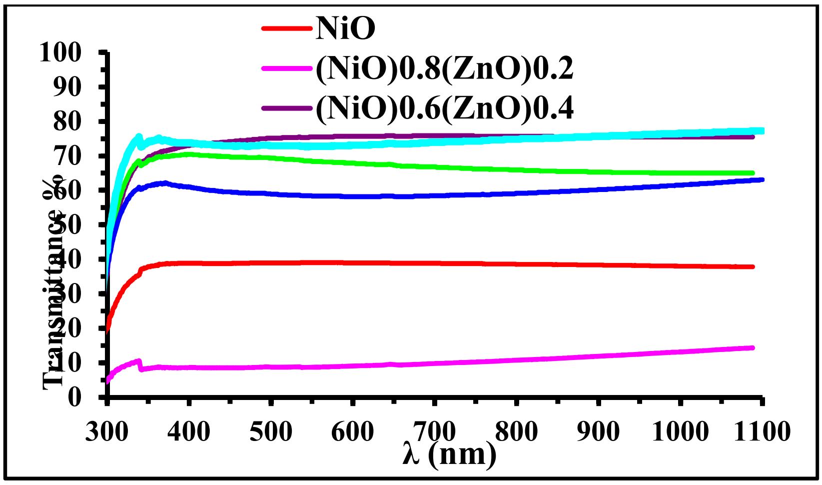

Figure 3. The transmittance spectrum with λ for $(NiO)_{1-x}(ZnO)_x$ Thin Films prepared by PLD technique.

Table 3. Illustrates the transmittance, absorption coefficient and optical constants at λ=550nm,and optical energy gap of $(NiO)_{1-x}(ZnO)_x$ thin films prepared by PLD technique.

Sample	*T%*	*α (cm⁻¹)*	*k*	*n*	*εr*	*εi*	*Eg(eV)*
x=0.0	*79.02*	*23548*	*0.094*	*1.976*	*3.896*	*0.370*	3.8
x=0.2	*54.41*	*60857*	*0.242*	*2.557*	*6.480*	*1.239*	3.7
x=0.4	*93.11*	*7139*	*0.028*	*1.484*	*2.200*	*0.084*	3.85
x=0.6	*91.25*	*9154*	*0.036*	*1.559*	*2.429*	*0.114*	3.95
x=0.8	*87.60*	*52969*	*0.211*	*1.695*	*2.829*	*0.715*	3.25

x=1.0	*92.42*	*7888*	*0.031*	*1.512*	*2.286*	*0.095*	3.3

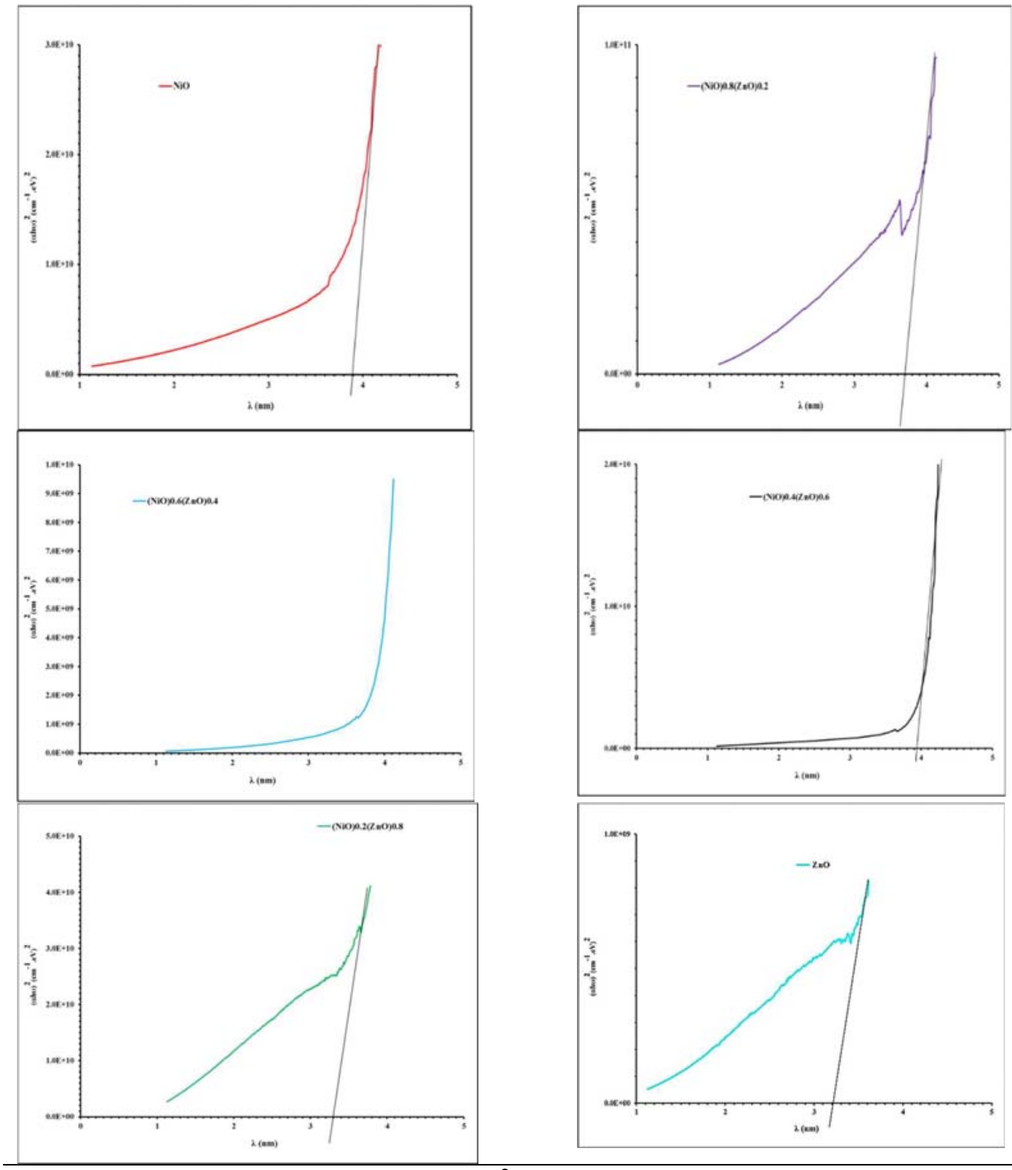

Figure 4. The plot diagram of $(\alpha h\upsilon)^2$ with $(h\upsilon)$ for $(NiO)_{1-x}(ZnO)_x$ thin films prepared by PLD technique.

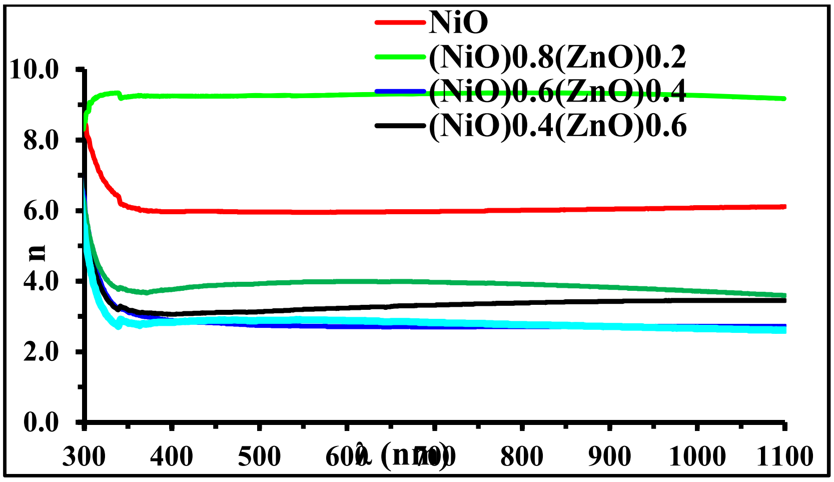

Figure 5. The plot diagram of n versus wavelength for $(NiO)_{1-x}(ZnO)_x$ thin films prepared by PLD technique.

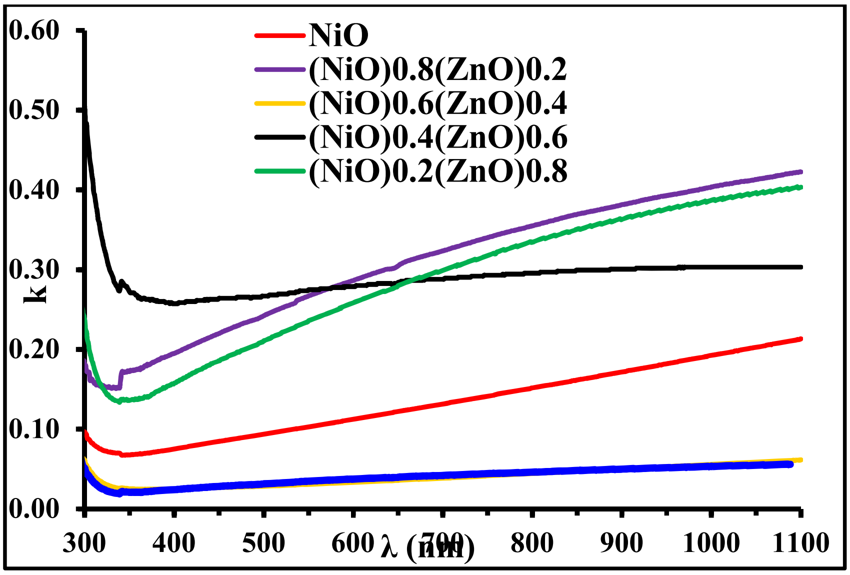

Figure 6. The plot diagram of k versus wavelength for $(NiO)_{1-x}(ZnO)_x$ fhin films prepared by PLD technique.

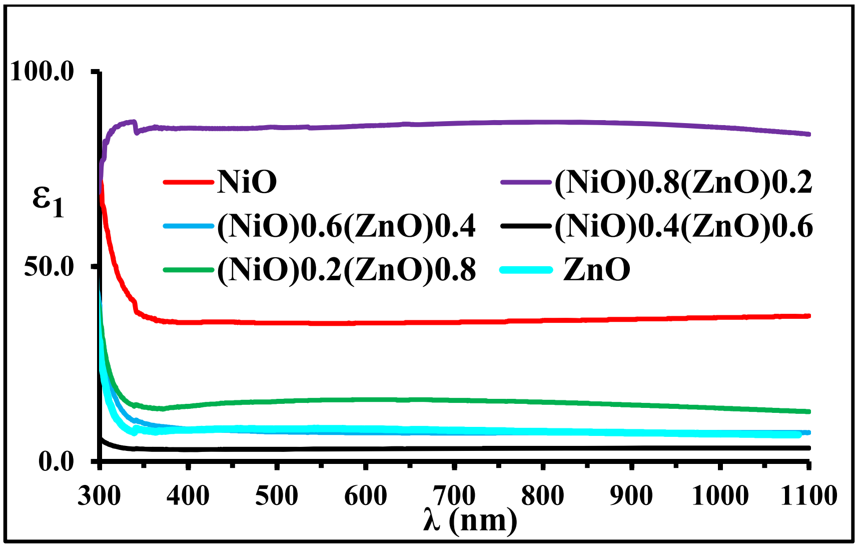

Figure 7. The plot diagram of ε_1 for $(NiO)_{1-x}(ZnO)_x$ Thin Films prepared by PLD technique.

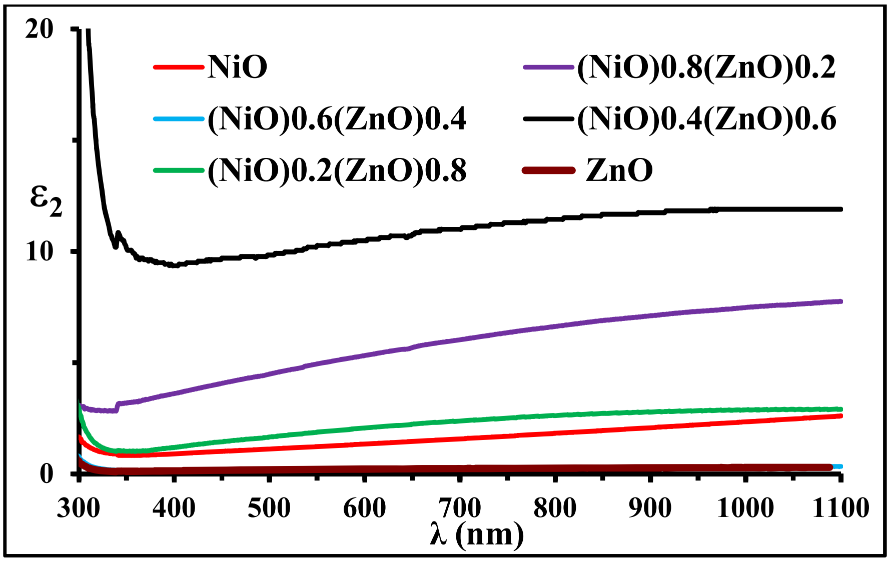

Figure 8. The plot diagram of ε_2 for $(NiO)_{1-x}(ZnO)_x$ thin films prepared by PLD technique.

4. Conclusions

1- All the ratio of $(NiO)_{1-x}(ZnO)_x$ compound and thin films have polycrystalline structure.
2- The highest energy gap was at $(NiO)_{0.6}(ZnO)_{0.4}$ while minimum energy gap attain at x=1.0 (ZnO).
3- Addition of ZnO to NiO oxide made the sample more transparent or less opaque to the incident light.
4- Addition of ZnO to NiO oxide reduced the energy gap as weel as all the optical constants.

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