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Effects of Copper Doping and Annealing Temperature on the Structural, Morphological and Optical Properties of NiO Thin Films

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The aim of this work is to study the influence of copper doping and annealing temperature treatment on structural, morphological and optical properties of nickel oxide (NiO) thin films. Cu doped NiO thin films were deposited on glass substrates at 350 °C by spray pyrolysis technique. Nickel chloride hexahydrate $NiCl_2{\cdot}6H_2O$, deionized water and copper were used as precursor, solvent and dopant source respectively after annealing at different temperatures of 400, 450, 500 and 550 °C. The grazing incidence X-ray diffraction (GIXRD) patterns revealed that NiO:Cu films are polycrystalline with face centered cubic structure and preferred orientation direction along [200] corresponding to 2θ value of approximately 43°. Atomic force microscopy (AFM) visualization revealed that surface morphology was found to be influenced by incorporation of Cu and average roughness increases from 5.17 nm to 99.03 nm when the doping rate varied from 2 % to 6 %. The optical transmittance decreases from 85 % to 65 % with the increase in Cu doping concentrations of NiO films annealed at 550 °C and the optical band gap was blue-shifted from 3.63 eV to 3.82 eV.

Keywords: Thin films, NiO, Spray pyrolysis, GIXRD, AFM, Optical properties.

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1. INTRODUCTION

Nickel oxide (NiO) is one of the most important group VIII-VI semiconductor materials. Having a wide band gap of 3.6-4.0 eV [1], it has NaCl structure type with octahedral Ni (II) and (O_2^-) sites, and the lattice parameter of 0.4176 nm [2]. NiO is an attractive material due to its various potential applications such as chemical sensors [3], antiferromagnetic layer [4], electrochromic display devices [5], catalyst for oxygen evolution [6], component of *p-n* junction diode [7], control of charge recombination in dye-sensitized solar cells [8], and photoelectrolysis [9]. It is apparent that to improve the properties of the films, it is necessary to optimize the conditions of preparation. NiO thin films have been prepared by various physical and chemical techniques, like chemical bath deposition [10], reactive sputtering [11], spray pyrolysis [12], sol-gel [13], pulsed laser deposition [14], electron beam evaporation [15] and others. Out of these techniques, spray pyrolysis is the most preferred to prepare NiO thin films due to its various advantageous features: less expensive manufacturing for large area coatings, better control of spray and low carrier gas flow, which permits to obtain films with very thin layers of uniform thickness [12].

In the present work, spray pyrolysis was employed to prepare copper doped NiO thin films. We present the effects of copper doping and annealing treatment on structural, morphological and optical properties of NiO thin films. All these results are compared with other works.

2. MATERIALS AND METHOD

2.1 Thin Film Preparation

Copper doped NiO thin films were successfully fabricated with various atomic concentrations of copper of 2, 4, 6 % on glass substrates having a dimensions of 1×26×10 mm³, which were cleaned by acetone during 10 min to eliminate any greasy track, then were dipped in ethanol during 10 min to remove microscopic dust, finally the substrates were washed with distilled water and then treated with ultrasound bath during 15 min before coating. The Cu doped NiO films with different Cu contents were deposited using spray pyrolysis apparatus HOLMARC Model HO-TH-04, a starting solution, containing nickel chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, 98.99 %, Biochem Chemopharma) used as precursor and copper (Cu, 99.8 %, MCSE) were dissolved in deionized water. Solution of 0.1 M with Cu/Ni ratio varied from 2 % to 6 % is sprayed via a nozzle assisted by compressed air as carrier gas onto the glass substrates at 350 °C, which undergoes evaporation, solute precipitation and pyrolytic decomposition, thereby resulting in the formation of NiO thin films according to the following reaction:

$$NiCl_2.6H_2O \xrightarrow{350^{\circ}C} NiO + 2HCl_{\uparrow} + 5H_2O_{\uparrow}\,.$$

In order to get uniform thin films, the substrate temperature, spray rate, distance from spray nozzle to substrates, spray angle and air pressure were kept constant at 350 °C, 200 μl/min, 12.5 cm, 90° and 2 bar respectively. The spraying process lasted 15 min. After the deposition for densification and crystallization, the films were placed into a programmable tube furnace MAGMA THERM and annealed at temperatures of 400, 450, 500 and 550 °C with a heating rate of 10 °C/min and holding time of 4 hours in dry air.

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2.2 Thin Films Characterization

The thickness of films was measured by a profilometer BRUKER Dektak XT and ranged from 290 nm to 440 nm. The structural properties were studied by X-ray diffractometer Inel EQUINOX 3000 (CuKα radiation, $\lambda = 1.54056$Å) with grazing incidence GIXRD. The morphology of the films was studied using atomic force microscope (AFM), Nano surf C3000 in tapping mode at room temperature. The transmittance and absorbance spectra of the films were recorded using SPECORD 210 plus UV/Vis/IR spectrophotometer in the wavelength range 190-1100 nm at the room temperature.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The GIXRD patterns of copper doped NiO films with various concentrations of copper of 2, 4 and 6 % annealed at different temperatures are shown in Fig. 1, Fig. 2 and Fig. 3 respectively, intensity data were collected over a range 2θ from 30° to 90° with the step width of 0.02° and a fixed incidence angle of 5°.

The variation of the lattice parameter, interplane spacing, mean grain size, microstrain and preferred orientation in the plane (hk0) for copper doped NiO thin films with various concentrations of 2, 4 and 6 % as a function of annealed temperatures are given in Table 1, Table 2 and Table 3 respectively. The relations used for calculating these parameters are similar to those described in Ref. [16]. The films doped with 2 % and 4 % which were deposited at 350 °C are amorphous in nature.

In Fig. 1 and Fig. 2 according to GIXRD study, the crystallinity of NiO films improved after annealing, and structure changed from amorphous phase into polycrystalline type characterized by five diffraction peaks at 2θ values of approximately 37°, 43°, 62°, 75° and 79° corresponding to (111), (200), (220), (311) and (222). Such improvement can be attributed to the removal of impurities such as chlorides, water vapors, etc. [12]. In comparison to the data from ICDD Card N°04-0835, all the diffraction peaks belong to NiO with face centered cubic structure showing [200] preferred orientation growth. The GIXRD patterns of the as-deposited and annealed copper doped NiO thin films with 6 % are shown in Fig. 3. The results indicate that the films are polycrystalline. The as-deposited films exhibit four weak diffraction peaks at scattering angles 2θ of 36.97°, 43.17°, 62.74° and 75.31° corresponding to (111), (200), (220) and (311), all the peaks belong to the cubic NiO phase. After annealing, another peak of NiO (222) has grown at an angle of 79.40°. All the films show the preferred orientation along the (200) plane. This result corresponds to that reported in literature [17].

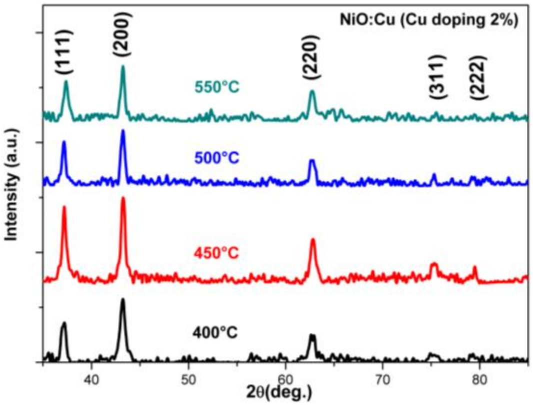

Fig. 1 – GIXRD patterns of NiO:Cu films (Cu doping 2 %) annealed at different temperatures

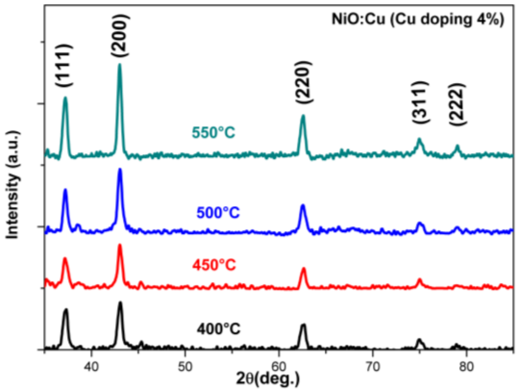

Fig. 2 – GIXRD patterns of NiO:Cu films (Cu doping 4 %) annealed at different temperatures

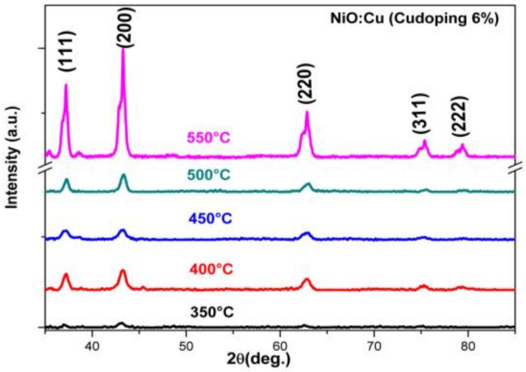

Fig. 3 – GIXRD patterns of NiO:Cu films (Cu doping 6 %) annealed at different temperatures

From Table 1 and Table 2, the average grain size increases and the microstrain decreases in copper doped NiO films with concentrations of 2 and 4 % as a function of annealing temperatures. The increase in intensity, smaller value of microstrain and larger average grain size indicate better crystallization. From the results of Fig. 3 and Table 3, the as-deposited films are of better crystalline quality.

Table 1 – Structural parameters for Cu doped NiO thin films (Cu doping 2 %) at different annealing temperatures

Temperature (°C)	2θ (deg.)	*hkl*	$d_{(hkl)}$ (Å)	*a* (Å)	β (deg.)	*D* (nm)	$\varepsilon \times 10^{-4}$	The preferred orientation plane (*hk*0)
400	37.091	(111)	2.421	4.109	0.991	10	34.758	*F* = 42 %
	43.170	(200)	2.090		0.932			
	62.742	(220)	1.482		0.691			
	75.234	(311)	1.261		0.541			
	79.321	(222)	1.204		0.421			
450	37.092	(111)	2.421	4.126	0.642	17	20.873	*F* = 35 %
	43.311	(200)	2.090		0.543			
	62.863	(220)	1.482		0.541			
	75.230	(311)	1.261		0.433			
	79.271	(222)	1.204		0.404			
500	37.092	(111)	2.421	4.184	0.481	21	17.882	*F* = 41 %
	43.169	(200)	2.101		0.433			
	62.850	(220)	1.482		0.424			
	75.316	(311)	1.261		0.397			
	79.631	(222)	1.204		0.381			
550	37.210	(111)	2.419	4.190	0.467	18	18.858	*F* = 43 %
	43.186	(200)	2.090		0.541			
	62.534	(220)	1.482		0.432			
	75.873	(311)	1.261		0.421			

Table 2 - Structural parameters for Cu doped NiO thin films (Cu doping 4 %) at different annealing temperatures

Temperature (°C)	2θ (deg.)	*hkl*	$d_{(hkl)}$ (Å)	*a* (Å)	β (deg.)	*D* (nm)	$\varepsilon \times 10^{-4}$	The preferred orientation plane (*hk*0)
400	37.423	(111)	2.401	4.183	0.775	12	29.170	*F* = 39 %
	43.011	(200)	2.102		0.487			
	62.911	(220)	1.476		0.835			
	75.048	(311)	1.265		0.911			
	79.220	(222)	1.208		0.956			
450	37.664	(111)	2.421	4.197	0.456	13	27.915	*F* = 41 %
	43.011	(200)	2.102		0.895			
	62.592	(220)	1.483		0.835			
	75.048	(311)	1.265		0.835			
	79.271	(222)	1.208		0.744			
500	37.273	(111)	2.410	4.189	0.624	15	24.991	*F* = 44 %
	43.011	(200)	2.101		0.502			
	62.612	(220)	1.482		0.956			
	75.197	(311)	1.262		0.644			
	79.079	(222)	1.210		0.644			
550	37.103	(111)	2.421	4.195	0.410	17	19.538	*F* = 44 %
	43.011	(200)	2.101		0.302			
	62.613	(220)	1.482		0.517			
	75.048	(311)	1.265		0.911			
	79.101	(222)	1.210		0.517			

Table 3 – Structural parameters for Cu doped NiO thin films (Cu doping 6 %) at different annealing temperatures

Temperature (°C)	2θ (deg.)	*hkl*	$d_{(hkl)}$ (Å)	*a* (Å)	β (deg.)	*D* (nm)	$\varepsilon \times 10^{-4}$	The preferred orientation plane (*hk*0)
As-deposited	36.967	(111)	2.430	4.193	0.418	16	23.568	*F* = 42 %
	43.170	(200)	2.094		0.807			
	62.744	(220)	1.485		0.567			
	75.307	(311)	1.261		0.687			
400	37.273	(111)	2.410	4.175	0.627	11	30.558	*F* = 36 %
	43.330	(200)	2.086		0.747			
	62.762	(220)	1.479		0.896			
	75.495	(311)	1.258		0.866			
	79.392	(222)	1.206		0.986			

450	37.273	(111)	2.410	4.174	0.538	8	36.587	*F* = 36 %
	43.330	(200)	2.080		0.657			
	63.060	(220)	1.473		0.896			
	75.517	(311)	1.256		0.747			
	79.548	(222)	1.202		1.105			
500	37.273	(111)	2.410	4.165	0.538	13	28.651	*F* = 44 %
	43.480	(200)	2.080		0.657			
	63.060	(220)	1.473		0.896			
	75.666	(311)	1.256		0.747			
	79.697	(222)	1.202		1.105			
550	37.273	(111)	2.410	4.175	0.538	12	26.08	*F* = 43 %
	43.330	(200)	2.086		0.478			
	62.890	(220)	1.477		0.866			
	75.346	(311)	1.260		0.836			
	79.399	(222)	1.206		0.836			

3.2 Morphological Properties

The surface roughness of copper doped NiO films was investigated by AFM. The average roughness R_a and the root mean square R_q parameters were calculated from AFM data using the following relations:

$$R_a = \frac{1}{l}\int_0^l |Z(x)|\,dx\,, \quad (1)$$

$$R_q = \sqrt{\frac{1}{l}\int_0^l Z^2(x)dx}\,, \quad (2)$$

where $Z(x)$ is the function that describes the surface profile analyzed in terms of height Z and position x of the sample over the evaluation length l. The results were collected in Table 4 with thickness measured by a profilometer as a function of Cu doping. From Table 4, it can be observed that, as Cu doping increases from 2 % to 6 %, the average roughness increases from 5.17 nm to 99.03 nm and the root mean square increases from 7.29 nm to 129.30 nm. The surface morphology was found to be influenced by incorporation of Cu, the crystallinity of copper doped NiO films improved and the average grain size decreased.

3.3 Optical Properties

The optical transmittance spectra of copper doped NiO films deposited with different Cu doping concentrations of 2, 4 and 6 % are displayed in Fig. 4, Fig. 5 and Fig. 6 respectively, in the wavelength range from 300 nm to 1100 nm. In Fig. 4, all the films display high transmittance in the visible and near infrared ranges.

The transmittance of copper doped NiO films increases with the increase of annealing temperatures from 67 % to 82 %. The increased transparency observed may be attributed to less scattering effects and better crystallinity. Fig. 5 shows that, the transmittance of the films increases with the increase in annealing temperatures up to 500 °C from 67 % to 77 %, and above this temperature it decreases. Fig. 6 indicates that, the highest optical transmittance is of the order of 75 % for copper doped NiO films at as-deposited temperature.

Transmittance of the copper doped NiO films decreases from approximately 82 % to 75 % with increase in Cu concentration from 2 % to 6 %. The decreased transmittance might be due to the surface morphology of copper doped NiO films with Cu concentration leading to more scattering. This result corresponds to that reported in literature [18].

The optical energy band gap E_g of copper doped NiO thin films may be estimated from the optical absorption spectra using the Tauc relationship as follows [16]:

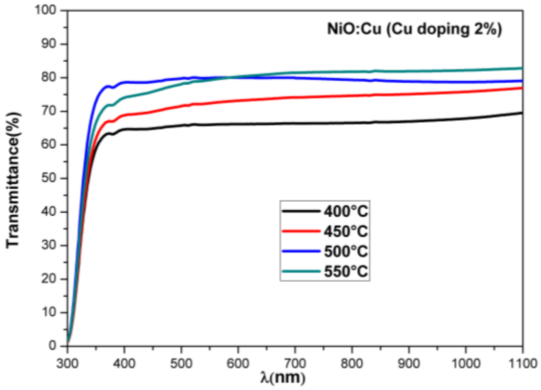

Fig. 4 – Optical transmittance spectra of NiO:Cu (Cu doping 2 %) as a function of annealing temperatures

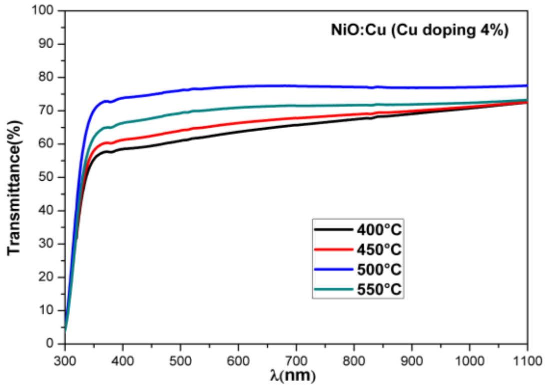

Fig. 5 – Optical transmittance spectra of NiO:Cu (Cu doping 4 %) as a function of annealing temperature

Table 4 – Surface roughness parameters and thickness of Cu doped NiO thin films as a function of concentration

Cu-doping concentration (%)	Annealing temperature (C°)	Thickness (nm)	R_a (nm)	R_q (nm)
2	550	290	5.17	7.29
4	550	415	9.43	11.96
6	As-deposited	338	26.37	30.32
	550	338	99.03	129.3

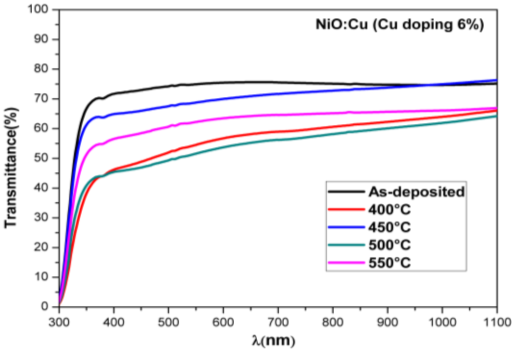

Fig. 6 – Optical transmittance spectra of NiO:Cu (Cu doping 6 %) as a function of annealing temperatures

$$\alpha h\nu = \mathrm{A}(h\nu - E_g)^n \,, \tag{3}$$

where α is the coefficient of absorption, $\alpha = 1/e$ $\ln(100/(T(\%))$, h is the Planck constant, ν is the frequency of light, A is the constant and n can take the values ½ or 2 for direct and indirect transitions of the electron from the valence band to the conduction band. The band gap energy of copper doped NiO films with 2, 4 and 6 % Cu concentrations was determined from the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ by extrapolating the linear region of $(\alpha h\nu)^{1/2}$ to the energy. Fig. 7 shows variation of energy band gap of NiO films with Cu concentrations of 2, 4 and 6 % as a function of annealing temperatures.

Also Urbach energy of the films can be determined by the following relation:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right), \tag{4}$$

where α_0 is a constant and E_u is the Urbach energy. The value of Urbach energy is calculated from the reciprocal value of the slope of the linear portion of $\ln\alpha$ versus $h\nu$. Fig. 8 shows variation of Urbach energy of NiO films with Cu concentrations of 2, 4 and 6 % as a function of annealing temperatures.

It can be seen that the band gap increases from 3.58 eV to 3.82 eV with increasing annealing temperature and copper concentration. The value of Urbach energy of NiO films with Cu concentration of 6 % decreases from 0.290 eV to 0.278 eV, this result can be explained by decrease in disorder in the films. The variation of the energy gap could be attributed to Burstien-Moss shift [19]. Increase in carrier concentration or decrease in defect states which is directly associated with improved crystallinity of the films, this observation agrees well with the results of Table 1, Table 2 and Table 3. These results are in good agreement with the reported in literature [17, 20].

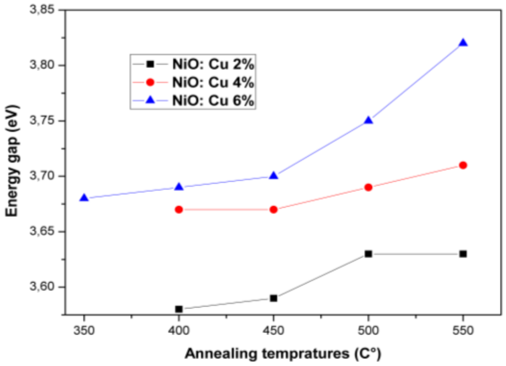

Fig. 7 – Variation of energy gap of NiO:Cu films as a function of annealing temperatures

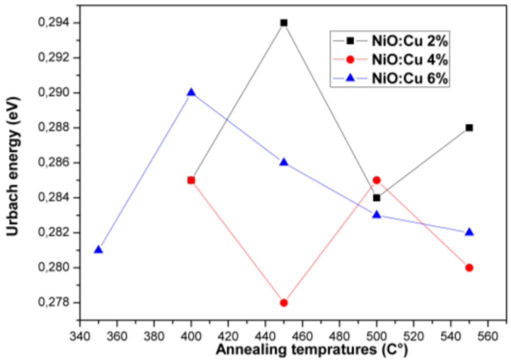

Fig. 8 – Variation of Urbach energy of NiO:Cu films as a function of annealing temperatures

4. CONCLUSIONS

In conclusion, copper doped NiO films were successfully deposited on glass substrates by spray pyrolysis technique. The influences of Cu doping and annealing treatment on structural, morphological and optical properties of copper doped NiO films were studied. The GIXRD analysis revealed that the films which were formed at 350 °C with Cu doping concentrations of 2 and 4 % were amorphous, while those deposited with Cu doping concentration of 6 % were polycrystalline. After thermal treatment, all the films became polycrystalline and exhibited face centered cubic crystal structure with [200] preferred orientation and the lattice parameter is about 4.17 Å. The increase in intensity, the smaller value of microstrain and larger average grain size indicate that the crystallinity was improved with increasing Cu doping and annealing temperatures. AFM visualization reveals that the Cu doping and annealing treatment have significant influence on the morphology of the films and the average roughness of surfaces increases from 5.17 nm to 99.03 nm that also confirms better crystallinity. Optical transmittance results showed that the films doped with Cu of 2 % and annealed at 550 °C have the highest transmittance in the visible range around 80 %, and it was higher than 65 % for the films doped with Cu of 4 and 6 % at the same annealing temperature. The optical transmittance was found to increase with annealing temperatures. However, the increase in Cu doping leads to the decrease of transmittance. The optical indirect band gap of NiO:Cu films increased from 3.58 eV to 3.82 eV with increase in Cu doping concentration.

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Вплив легування міддю та температури відпалу на структурні, морфологічні та оптичні властивості тонких плівок NiO

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Метою даної роботи є вивчення впливу легування міддю та температури відпалу на структурні, морфологічні та оптичні властивості тонких плівок оксиду нікелю (NiO). Тонкі плівки NiO, леговані Cu, були нанесені на скляні підкладки при температурі 350 °C методом спрей-піролізу. Гексагідрат хлориду нікелю $NiCl_2{\cdot}6H_2O$, деіонізована вода та мідь використовувались відповідно як прекурсор, розчинник та домішка після відпалу плівок при температурах 400, 450, 500 та 550 °C. Рентгенівські дифрактограми (GIXRD) показали, що плівки NiO:Cu є полікристалічними з ГЦК структурою та переважним напрямком орієнтації вздовж [200], що відповідає значенню 2θ приблизно 43°. Візуалізація атомно-силової мікроскопії (AFM) виявила, що на поверхневу морфологію впливає додавання Cu, а середня шорсткість збільшується від 5,17 нм до 99,03 нм, коли швидкість легування змінюється від 2 % до 6 %. Оптичний коефіцієнт пропускання зменшується з 85 % до 65 % при збільшенні концентрації легування міддю плівок NiO, відпалених при 550 °C, а оптична ширина забороненої зони зміщується у синій діапазон з 3,63 еВ до 3,82 еВ.

Ключові слова: Тонкі плівки, NiO, Спрей-піроліз, GIXRD, AFM, Оптичні властивості.