Structural and morphological studies of $(\text{NiO})_{1-x}(\text{CuO})_x$ Thin Films Prepared by Chemical Spray Paralysis Technique

Nahida B. Hasan, Mohammed Jasim Mohammed

Department of Physics, College of Science, University of Babylon

E-mail address: moh_mansory2002@yahoo.com

Keywords: Spray pyrolysis, Nickel oxide, Copper oxide , Structural properties , Thin films.

ABSTRACT. $(\text{NiO})_{1-x}(\text{CuO})_x$ Thin Films have been deposited on glass substrates by chemical spray paralysis technique for with different ratios at temperature $(375 \pm 10)^\circ\text{C}$ with spray rate 4s./1min. The structural properties of thin films have been investigated by the study of X-Ray diffraction analysis and morphological by study atomic forces microscope (AFM) . From the XRD result showed all samples are polycrystalline and various structural parameters were calculated. all the films show most preferred orientation along (111), (200) and (220) planes. The (AFM) results shows that the roughness decreases with mixing ratios.

1. INTRODUCTION

There are various techniques for the preparation of thin films but chemical spray paralysis technique has been largely used for the preparation of thin films. This method is summarized by spraying the solution of the chosen chemical material on hot substrate to form thin film on it [1]. This is the easiest method comparing with the others, this method was used by Chamberlain and Skarman in 1966 [2]. The advantages of the chemical spray pyrolysis technique are summarized by Low cost comparing with the other methods, Easy and fast in preparing thin film, The possibility of getting wide area thin film with a suitable thickness and high stability in time with its physical property[3].

Nickel oxide NiO of semiconductor compounds and the group is (II-VI) of the periodic Table [4]. And has a crystalline structure of the rock salt kind of structure of sodium chloride salt (NaCl)[5]. These nickel oxide NiO has cubic (NaCl-like FCC) structure and pale green color. The FCC structure is having lattice parameter of 0.4195 nm with slight triangular distortions at low temperatures. The stoichiometry of NiO is roughly indicated by the color of the sample . The color of the NiO is highly sensitive to the presence of higher valence states of nickel even in traces. It exhibits widely varying magnetic, optical, electronic and electrochemical properties depending on synthesis process and resultant defect structure [6]. The unit cell of a centralized faceted type (FCC) and the bond that connects between the nickel oxide ions are covalent bond resulting from the participation of two electrons between the nickel atoms and oxygen atoms [7]. The material nickel oxide from the transparent conductive oxides (TCO) which have high conductivity and lighting gap energy directly ,the width of energy gap 3.5 eV at 300K so that the cutter wavelength of 354 nm in the violet end of the spectrum region [8], we can deduce from this that film absorbency be at the wavelength of violet, while the long-wavelength be window.

NiO is one of these oxides and last years, a growing interest has been devoted to nickel oxide thin films. Due to its high chemical stability, as well as optical magnetic and electrical properties, NiO has a wide range of applications such as films for electro chromic devices, organic light emitting diodes, chemical sensors, n-p junction electrodes in dye sensitized solar cells and p-type large band gap oxide [9].

In recent years, cupric oxide (CuO) has attracted increasing interest for its prospective applications in many fields. As an important low cost and non-toxic transition metal oxide with a narrow band gap of ~ 1.2 eV at room temperature[10]. CuO is a p-type semiconductor with monoclinic crystalline structure and cell parameters $a = 0.4684$ nm, $b = 0.3423$ nm, $c = 0.5128$ nm and $\beta = 99.54^\circ$. Its energy gap is in the range 1.21-1.51 eV. This is an attractive system for many researchers due to its

photoconductive and photo-thermal applications and for studies of the transport mechanism in cuprates with high-TC superconductivity. copper oxide films have received much attention for its various applications some of which are in catalysis, semiconductors, batteries, gas sensors, biosensors, magnetic storage media, solar cells, electronics, varistors, capacitors and field transistors. Because the chemical and physical properties of CuO are strictly dependant of its morphology, in recent years considerable efforts have been made to synthesize various types of CuO nanostructures. Copper oxide has been dark brown inclined to the black odorless[11].

2-EXPERIMENTAL DETAILS

$(\text{NiO})_{1-x}(\text{CuO})_x$ consists of mixing two compounds nickel oxide and copper oxide with different ratios, at first prepare NiO and CuO compounds severally. NiO solution was prepared by dissolving of $(\text{NiCl}_2 \cdot 6\text{H}_2\text{O})$ [which is a powder of green color, it's molecular weight 237.69 g/mol] in 50 ml distilled water at room temperature, a magnetic stirrer is incorporated for this purpose for about (30) minutes to facilitate the complete dissolution of the solute in the solvent as shown in equation (1) [12]:

Also CuO can preparing of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ [which is a powder of green color it's molecular weight 199.65 g/mol] in 100 ml distilled water and using magnetic stirrer too according to the following reaction in equation (2) [13]:

When preparing NiO and CuO solvents mixing the solutions with different ratios as shown in Table (1) according the following relation:

Table (1):The mixing ratios for $(\text{NiO})_{1-x}(\text{CuO})_x$ thin films.

X (ml)	NiO_{1-x}	CuO_x	$\text{NiO}_{1-x} \text{ CuO}_x$
0	NiO	0	NiO_{pure}
0.2	$\text{NiO}_{0.8}$	$\text{CuO}_{0.2}$	$\text{NiO}_{0.8} \text{ CuO}_{0.2}$
0.4	$\text{NiO}_{0.6}$	$\text{CuO}_{0.4}$	$\text{NiO}_{0.6} \text{ CuO}_{0.4}$
0.6	$\text{NiO}_{0.4}$	$\text{CuO}_{0.6}$	$\text{NiO}_{0.4} \text{ CuO}_{0.6}$
0.8	$\text{NiO}_{0.2}$	$\text{CuO}_{0.8}$	$\text{NiO}_{0.2} \text{ CuO}_{0.8}$
1	0	CuO	CuO_{pure}

The resulting solution from these mixing ratios putting on magnetic stirrer about (10-20) minutes to homogeneity.

3. RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD)

XRD pattern of $(\text{NiO})_{1-x}(\text{CuO})_x$ thin film prepared by spray pyrolysis technique at substrate temperature of (375°C) have been shown in figures (4-1 a,b,c,d,e,f). The peaks of the XRD were observed between $2\theta = 0^\circ$ and $2\theta = 70^\circ$. These films showed a crystal structure of the films was identified to be polycrystalline, and this is agreement with [14,15, 16].

The results showed there is obvious effect on the crystal structure at mixing, thus there is a shifted slightly in peaks position and the Table (1) shows peaks position for all pure and mixing films. Also can be calculate the following values :

1- Interlayer spacing between the crystalline planes (d)

It calculated for all preparing films by using Bragg's law .We found that the results are approach for the standard values[17] .

$$n\lambda = 2d \sin\theta \quad (4)$$

where $\lambda = 0.154 \text{ nm}$ and θ is Bragg's angle of XRD peak.

2- The Grain Size (G.S)

The grain size of the films was calculated for all peaks using the Scherrer's formula[18].

$$G.S = \frac{0.9\lambda}{\beta \cos \theta} \quad (5)$$

where β = full width at half maximum (FWHM) measuring by radian angels.From the Table (2) found the average grain size for $(\text{NiO})_{\text{pure}}$ and $(\text{CuO})_{\text{pure}}$ equal to 40.61 nm and 36.76 nm respectively, while its observed the average grain size of the mixing films for all ratios is decreased with increasing the mixing ratios, this is a reason of the radii of Cu^{+2} is (0.69 Å) less than of ionic radii of Ni^{+2} (0.78Å) each Cu ion could substitute one host cation. However, assuming that copper oxide exists in the form of CuO, the substitution process should not be accompanied by any change in the oxidation state of NiO [19].

3- Micro strain (ϵ)

Its calculated by the equation (3), from the Table (2) can be seen the average micro strain for NiO_{pure} and CuO_{pure} equle to 0.086 % and 0.094% respectively.

$$\epsilon = \frac{\beta \cos \theta}{4} \quad (6)$$

Also can be observed that the average micro strain for mixing films is increase with decrease the average grain size, the strain is increased in NiO when its formed mixture with CuO. This may be due to the accumulation of CuO on the grain boundary of NiO which inhibit the crystal growth and leads to strain generation in NiO grains [20].

Figure (1):XRD-graph for (a) NiO_{pure} , (b) $\text{NiO}_{0.8}\text{CuO}_{0.2}$, (c) $\text{NiO}_{0.6}\text{CuO}_{0.4}$ (d) $\text{NiO}_{0.4}\text{CuO}_{0.6}$, (e) $\text{NiO}_{0.2}\text{CuO}_{0.8}$ and (f) CuO_{pure}

Table (2): The obtained result of the structural parameters from XRD for $(\text{NiO})_{1-x}(\text{CuO})_x$ thin film.

Sample	2θ (deg)	θ (deg)	d_{standard} (nm)	$d_{\text{experimental}}$ (nm)	micro strain (ϵ) 10^{-3}	Average Strain	hkl	G.S (nm)	Average G.S (nm)
NiO_{pure}	37.17	18.58	0.2413	0.24203	0.0849	0.086	(111)	40.77	40.61
	43.49	21.74	0.2091	0.20821	0.1001		(200)	34.61	
	62.64	31.32	0.1477	0.14838	0.0745		(202)	46.47	
$\text{NiO}_{0.8}\text{CuO}_{0.2}$	37.48	18.74	0.2399	0.24009	0.0668	0.075	(111)	51.86	46.97
	38.49	19.24	0.2336	0.23402	0.0659		(111)*	52.57	
	43.47	21.51	0.2080	0.2083	0.0948		(200)	36.50	
$\text{NiO}_{0.6}\text{CuO}_{0.4}$	37.31	18.65	0.2407	0.24115	0.0735	0.109	(111)	47.08	34.21
	38.22	19.11	0.2352	0.32722	0.1100		(111)*	31.57	
	43.47	21.73	0.2080	0.2083	0.1447		(200)	23.99	
$\text{NiO}_{0.4}\text{CuO}_{0.6}$	37.62	18.81	0.2388	0.23923	0.0845	0.12	(111)	40.96	31.88
	38.28	19.14	0.2349	0.23526	0.1978		(111)*	17.51	
	43.55	21.83	0.2071	0.20743	0.0931		(200)	37.19	
$\text{NiO}_{0.2}\text{CuO}_{0.8}$	35.5	17.75	0.2526	0.2530	0.1298	0.13	(11 $\bar{1}$)	26.84	37.43
	38.79	19.39	0.2319	0.2322	0.1975		(111)*	17.53	
	43.21	21.60	0.2092	0.2094	0.1054		(200)	32.85	
CuO_{pure}	35.47	17.73	0.2533	0.25323	0.0997	0.094	(11 $\bar{1}$)	34.74	36.76
	38.15	19.19	0.2348	0.23467	0.0896		(111)*	38.65	
	52.56	26.28	0.1738	0.17421	0.0938		(020)	36.90	

3.2 Atomic Force Microscope (AFM)

The topography study of the surface to the prepared films and the effect of mixing ratio used Atomic Force Microscope (AFM) with the ability to depiction and analysis of these surfaces and give the statistical values with high accuracy about surface roughness values depending on the Root Mean Square (RMS) of the average roughness. Through microscopic analysis (AFM) we can study the effect of (thickness, concentration, temperature, method of preparation etc.) on the properties of the deposited film material to the fact that the study of the surfaces of film materials important to recognize how the distribution and arrangement of atoms on surfaces, and to identify the differences or homogeneity properties or attributes relating to each atom separately and illustrative image about the distribution rate of the crystalline size onto surfaces [21].

Figures (2-1,2,3) shows the AFM images within the scanning area ($1800 \times 1800 \text{ nm}$) and analytical ability (pixels = 612,612) of all samples deposited at substrate from glass with temperatures of $T_s = 375^\circ \text{C}$.

Figure (2-1 a,b,c,d,e,f) shows a diagram of distribution of growth granular gropes on the surfaces of the deposited films, Table (4-2) shows that the average diameters (grain size) of $(\text{NiO})_{\text{pure}}$ and $(\text{CuO})_{\text{pure}}$ thin films are (83.54 and 80.78 nm) respectively that agreement with [12, 22] and the average diameters (grain size) for $(\text{NiO})_{1-x}(\text{CuO})_x$ are (91.88, 88.66, 79.65, 77.92 nm) for $X = (0.2, 0.4, 0.6 \text{ and } 0.8)$ respectively. We observed decreases the grain size with increase the mixing ratios this lead to surface homogeneity.

Figure (2-2 a,b,c,d,e,f) shows image of AFM in 2-Dimensions its found surface roughness rate and the root mean square RMS (the sum of the highs and lows of surface squared divided by the sum of the total number under the square root) of the deposited films , from Table (3) shows the roughness for $(\text{NiO}_{\text{pure}})$ and $(\text{CuO}_{\text{pure}})$ films are (2.03, 1.73 nm) and the root mean square RMS equal to (2.5, 2.18 nm) respectively, also the roughness and the root mean square RMS for $(\text{NiO})_{1-x}(\text{CuO})_x$ are (1.25, 0.612, 0.292, 2.89), (1.56, 0.753, 0.373, 3.64) for $(X = 0.2, 0.4, 0.6 \text{ and } 0.8)$ respectively, the first three results decreases in roughness rate and the root mean square RMS with increases the mixing ratios it obvious that surface is smooth, the increase of root mean square in last result lead to increase crystalline growth in vertical direction more than horizontal direction [21].

Figure (2-3 a,b,c,d,e,f) shows image in 3-Dimension of prepared thin film. This image was found that the surface thickness of the thin films value in figure (2-3 a,b,c,d) observed decreases in thickness which mean getting homogeneous crystalline growth along horizontal direction lead to uniform granular surface morphology thin film, while figure (2-3e) the crystalline defects have led to get un uniform granular surface morphology thin film.

Table (3): The grain size, roughness and RMS of $(\text{NiO})_{1-x}(\text{CuO})_x$ preparing thin films.

Sample	RMS (nm)	Roughness (nm)	Average Gran size (nm)
NiO_{pure}	2.5	2.03	83.54
$\text{NiO}_{0.8}\text{CuO}_{0.2}$	1.56	1.25	91.88
$\text{NiO}_{0.6}\text{CuO}_{0.4}$	0.753	0.612	88.66
$\text{NiO}_{0.4}\text{CuO}_{0.6}$	0.373	0.292	79.65
$\text{NiO}_{0.2}\text{CuO}_{0.8}$	3.64	2.89	77.92
CuO_{pure}	2.18	1.73	80.78

Figure (2-1): diagrams of granularity distribution for a: NiO_{pure} , b: $\text{NiO}_{0.8}\text{CuO}_{0.2}$, c: $\text{NiO}_{0.6}\text{CuO}_{0.4}$ d: $\text{NiO}_{0.4}\text{CuO}_{0.6}$, e: $\text{NiO}_{0.2}\text{CuO}_{0.8}$ and f: CuO_{pure}

Figure (2-2): 2-D analytical images for a: NiO_{pure}, b: NiO_{0.8}CuO_{0.2}, c: NiO_{0.6}CuO_{0.4} d: NiO_{0.4}CuO_{0.6}, e: NiO_{0.2}CuO_{0.8} and f: CuO_{pure}.

Figure (2-3): 3-D analytical images for a: NiO_{pure} , b: $\text{NiO}_{0.8}\text{CuO}_{0.2}$, c: $\text{NiO}_{0.6}\text{CuO}_{0.4}$ d: $\text{NiO}_{0.4}\text{CuO}_{0.6}$, e: $\text{NiO}_{0.2}\text{CuO}_{0.8}$ and f: CuO_{pure} .

4.CONCLUSIONS

The (XRD) measuring of $(\text{NiO})_{1-x}(\text{CuO})_x$ thin films showed its polycrystalline cubic type and decreasing the peak intensity in preferred direction (111) and deviation (2θ) with in obvious decreased in the average grain size reach to (31nm).AFM image showed the RMS, roughness and average grain size decreases with increases the mixing ratio.

References

- [1] R. R. Chamberlin and J. S. Skaarman, " Chemically sprayed thin film Photovoltaic converters", *Solid State Electron*, Vol.9, pp.819-823, (1966).
- [2] S.M.Sabnis, Prakash A. Bhadane and P. G. Kulkarni, " Process Flow of Spray Pyrolysis Technique ", *Journal of Applied Physics*, Vol. 4, pp. 7-11, (2013).
- [3] Marko Nieuwenhuizen (project leader), Jaap Bastiaansen (treasurer), Brian Pauw, Xin Wang, Karen Scholz (tutor), Jetse Reijenga (coordinator),"The versatility of nickel oxide, from rechargeable batteries to smart windows and electrocatalysts", Interfaculty Project Marko. June 23, (2004).
- [4] E. Fujii, A. Tomozawa, H. Torii, and R. Takayama, "Preferred orientations of NiO films prepared by plasma-enhanced metalorganic chemical vapor deposition,"*Japanese Journal of Applied Physics*, Vol. 35, pp. L328–L330, (1996).
- [5] P. Potapov and D. Schryvers, EMAT, University of Antwerp, RUCA, Groenenborgerlaan 171, B-2020 Antwerp, Belgium, *Physical Review B*, 69, 184404 (2004).
- [6] J.D. Desai, Sun-Ki Min, Kwang-Deog Jung, Oh-Shim Joo," Spray pyrolytic synthesis of large area NiO_x thin films from aqueous nickel acetate solutions", *Applied Surface Science* ,Vol. 253, pp.1781–1786, (2006).
- [7] G. Benedek, L. Reining, M. Gatti," Exchange and Correlation effects in the electronic properties of transition metal oxides: the example of NiO ", *Anno Accademico*, (2008).
- [8] M. Guziewicz, W. Junga, J. Grochowska, M. Borysiewicz, K. Golaszewska, R. Kruszkaa, A. Baranska, A. Piotrowska, B.S. Witkowskib, J.Z. Domagala;b,M. Gryzinski, K. Tyminski and A. Stoner, Institute of Electron Technology, al. Lotników ,Vol.120, 32/46, 02-668, Poland, (2012).
- [9] B.A. Reguig, A. Khelil, L. Cattin, M. Morsli, J.C. Bernède " Properties of NiO thin films deposited by intermittent spray pyrolysis process", *Applied Surface Science*, Vol. 253, pp. 4330–4334, (2007) .
- [10] F. Bayansal, H.A. C. etinkara, S. Kahraman, H.M. C. akmak, H.S. Gu'der "Nano-structured CuO films prepared by simple solution methods: Plate-like, needle-like and network-like architectures", *Ceramics International*, Vol. 38, pp.1859–1866, (2012).
- [11] L.De Los Santos Valladares , D. Hurtado Salinas , A. Bustamante Dominguez , D. Acosta Najarro,S.I. Khondaker , T. Mitrelias, C.H.W. Barnes , J. Albino Aguiar and Y. Majima "Crystallization and electrical resistivity of Cu₂O and CuO obtained by thermal oxidation of Cu thin films on SiO₂/Si substrates" , *Thin Solid Films*, Vol. 520, pp. 6368–6374 (2012).
- [12] Ratnesh Sharma, A.D. Acharya, S.B. Shrivastava, T. Shripath and V. Ganesan," Preparation and characterization of transparent NiO thin films deposited by spray pyrolysis technique",*Optik*, Vol. 125, pp. 6751–6756, (2014).
- [13] S.S. Falahatgar, F.E. Ghodsi, F.Z. Tepehan, G.G. Tepehan and I. Turhan," Electrochromic performance, wettability and optical study of coppermanganese oxide thin films: Effect of annealing temperature", *Applied Surface Science*, Vol. 289, pp. 289– 299, (2014).
- [14] A.Madhavi, Ch. Seshendra Reddy, N. V. Ravindra, P. Lokesh and P. Sreedhara Reddy," Effect of Substrate Temperature on the Structural, Optical and Electrical Properties of Electron Beam Evaporated NiO Thin Films", *International Journal of Advanced Research in Physical Science (IJARPS)*, Vol. 1, pp.16-20, (2014).
- [15] Abdul Hai Alami, Anis Allagui & Hussain Alawadhi," microstructural and optical studies of CuO thin films prepared by chemical ageing of copper substrate in alkaline ammonia solution", *Journal of Alloys and Compounds* ,Vol. 617, pp.542–546, (2014).
- [16] A. Yildiz S, . Horzum, N. Serin, T. Serin"Hopping conduction in In-doped CuO thin films", *Applied Surface Science*, Vol.318, pp.150-107, (2014).
- [17] Y. Sirotnin and M. Shaskolskya, "Fundamental of Crystal Physics", Mir Pub., Moscow (1982).
- [18] A.J.C.Wilson,"X-Ray optics",London Methnen and coltd New York John,Wiley and Sons INC, pp. 1-5, (1962).

-
- [19] A.M. Turkey," Electrical surface and catalytic properties of NiO asinfluenced by doping with CuO and Ag₂O",*Applied Catalysis A: General*, Vol. 247, pp.83–93, (2003).
- [20] P. Mallick and C. S. Sahoo," Effect of CuO Addition on the Structural and Optical Properties of NiO Nanoparticles" , *Nanoscience and Nanotechnology*, Vol .3, pp.52-55, (2013).
- [21] Ghada Ayad Kadhim AL-Lamy," Fabrication and Study the Optoelectronics Properties of Detector NiO/c-Si by Spray Pyrolysis Technique", M.Sc.Thesis, Baghdad University (2013).
- [22] T. Serin, A.Yildiz, S- .H. S-ahin, N.Serin ," Multiphonon hopping of carriers in CuO thin films" *Physica B* ,Vol. 406, pp.3551–3555, (2011).