Spray Pyrolysis Deposition and Effect of Annealing Temperature on Optical Properties of Cu:NiO Film

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ABSTRACT
Spray pyrolysis method that used to prepare Cu:NiO thin films onto glass substrate with various annealing temperature. Spectral transmittance of prepared thin films determined by UV-Visible spectrophotometer in the range of (380-900) nm. The transmittance decreased with increasing annealing temperature. While the absorption coefficient and extinction coefficient increased with increasing annealing temperature. Energy gap decreased from 2.9 eV before annealing to 2.78 eV after 500 ºC annealing temperature.

Keywords: Cu; NiO; thin film; optical properties; Energy gap

1. INTRODUCTION
Transparent conducting oxides (TCO) thin films are attracting more and more attention due to their widely applications such as liquid crystal displays, light-emitting diodes, solar cells and detector[1-2]. In the literature, the optical band gaps of bulk NiO is 4 eV [3-5]. Due to the wide band gap 3.6-4 eV, it has a wide range of applications in optoelectronics as well as in thermal applications [6]. Metal oxides like nickel oxides have found wide application in materials applications such sensors [7], transparent electrode [8], efficient control of energy inflow-outflow of buildings or automobiles and aerospace [8-9], large scale optical switching glazing and electronic information display [10]. Several physical and chemical methods, such as sputtering [11], pulsed laser deposition [12], chemical bath deposition [11-13] and sol-gel [14] have been used to obtain nickel oxide films. All the NiO thin film prepared methods offer different advantages depending on the application of interest and many efforts have been conducted to obtain films with the desirable physical and/or chemical properties [15].

In the present work, the effect of annealing temperature on the optical properties of Cu-doped NiO films deposited by chemical spray pyrolysis is considered.

2. EXPERIMENTAL DETAILS
Thin films of NiO doped by Cu were prepared using chemical spray pyrolysis method. The coating solution was made by dissolving nickel chloride hexahydrate (NiCl2.6H2O)
(from sigma-Aldrich company), into 100 ml of redistilled water to make 0.1 M solution. The volumetric ratio of Cu was 4% and substrate temperature was 380 ºC. The layers have been deposited onto glass substrates that are cleaned in distilled water and then dried using air blower. After that they were cleaned again with acetone in order to remove any strains on it. In order to optimize the deposition arriving at the following conditions; spraying rate 0.2 ml/spray, substrate to nozzle 30 cm, spraying time during each cycle 7 sec, time interval between successive sprays 1.5 min, and the carrier gas (filtered compressed air) was maintained at a pressure of 105 Nm-2.

Thicknesses of the films were measured gravimetrically and the measured thickness is about 300 nm. The prepared films were annealed at 450 and 500 ºC, the optical transmittance and absorbance were recorded in the wavelength range (380-900 nm) using UV-Visible spectrophotometer (Shimadzu Company Japan) double beam spectrophotometer.

3. RESULTS AND DISCUSSION

The transmittance spectra of Cu-doped NiO thin film for various annealing temperature have been recorded by UV-Visible spectrophotometer as in Fig.1. From this figure, it can notice that the transmittance decreases with increasing annealing temperature for all deposited thin films.

![Fig. 1. The transmittance spectra versus wavelength of Cu:NiO thin film.](image)

The absorption coefficient ($\alpha$) is defined as the ability of a material to absorb the light of a given wavelength, and is measured from the following relation [16]:

$$\alpha = \frac{2.303A}{d}$$  \hspace{1cm} (1)

where A is the absorbance and d is the thickness of the film. The relationship between $\alpha$ and wavelength ($\lambda$) shown in Fig.2. From this figure, it can notice that the absorption...
coefficient increases with increasing annealing temperature for all deposited Cu:NiO thin films.

![Graph of absorption coefficient versus photon energy](image)

**Fig. 2.** The absorption coefficient versus photon energy of Cu:NiO thin film.

The correlation between absorption coefficient and optical band gap $E_g$, as expressed by the following relation [17]:

$$\alpha \nu = (\nu - E_g)^n \quad (2)$$

Where $\nu$ is the photon energy and $n$ is $1/2$ for direct inter band transitions or $2$ for indirect inter band transitions. Portion of the graph of $(\alpha \nu)^n$ against $\nu$ is extrapolated to $\alpha=0$ the intercept gives the transition band gaps as in Figs 3-5. From these figures, it can notice that the energy gap decreases with increasing annealing temperature from $2.9 \text{ eV}$ before annealing to $2.78 \text{ eV}$ after $500 \, ^\circ\text{C}$ annealing temperature.
Fig. 3. Variation of $(\alpha h \nu)^2$ with photon energy of Cu:NiO thin film before annealing.

Fig. 4. Variation of $(\alpha h \nu)^2$ with photon energy of Cu:NiO thin film after 450 °C annealing temperature.
Fig. 5. Variation of $(\alpha h\nu)^2$ with photon energy of Cu:NiO thin film after 500 °C annealing temperature.

Fig. 6. The extinction coefficient versus wavelength of Cu:NiO thin film.

The refractive index ($n$) depend on the reflectance ($R$) and extinction coefficient as in the following relation [20]:

$$n = \left[\left(\frac{4R}{(R-1)^2}\right) - K_0^2\right]^{\frac{1}{2}} - \frac{R + 1}{R - 1}$$

(4)
Fig. 7 represent the relationship between refractive index and wavelength for Cu-doped NiO thin film for various annealing temperature. From this figure, it can notice that the refractive index decreases with increasing annealing temperature until 550 nm, and then the refractive index change slightly at wavelength greater than 550 nm.

4. CONCLUSION

Spray pyrolysis method that used to prepare Cu:NiO thin films onto glass substrate with various annealing temperature. The transmittance decreased with increasing annealing temperature. While the absorption coefficient and extinction coefficient increased with increasing annealing temperature. The refractive index takes various behaviors with wavelength. Energy gap decreased from 2.9 eV before annealing to 2.78 eV after 500 ºC annealing temperature.

References

[1] J. F. Wager, “Transparent electronics”, *Science* **300** (2003) 1245–1246.
[2] H. Hosono, H. Ohta, M. Orita, K. Ueda, and M. Hirano, “Frontier of transparent conductive oxide thin films”, *Vacuum* **66** (2002) 419–425.
[3] Z. M. Jarzebski, Oxide Semiconductors, Pergamon Press, Poland, 1973.
[4] P. Puspharajah, S. Radhakrishna, A. K. Arof, *J. Mater. Sci.* **32** (1997) 3001-3006.
[5] A. Gupta, H. S. Bhatti, D. Kumar, N. K. Verma, R. P. Tandon, Digest J. *Nanomater. Biostruct.* **1** (2006) 1-9.
[6] A. R. Balu, U. S. Nagarethinam, "nanocrystalline NiO thin films prepared by a low cost simplified spray technique using perfume atomizer", *Journal of electron devices* 13(2012).

[7] D. Mutschall, S. A. Berger, and E. Obermeier, Proc. of 6th international meeting on chemical sensors, Gaithersburg, 28 (1996).

[8] M. Fantini and A. Gorenstein *Solar Energy Materials* 16 (1987)487.

[9] M. K. Carpenter, R.S. Conell, and D.A. Corrigan, Solar Energy Material. (1987)16333.

[10] P. C. Yu, G. Nazri and C. M. Lampert, *Solar Energy Materials*. 16 (1987) 1.

[11] A. Mendoza-Galván, M. A. Vidales-Hurtado and A. M. López-Beltrán, “Comparison of the Optical and Structural Properties of Nickel Oxide-Based Thin Films Obtained by Chemical Bath and Sputtering,” *Thin Solid Films* 517 (2009) 3115-3120.

[12] I. Valyukh, S. Green, H. Arwin, G. A. Niklasson, E. Wäckelgård and C. G. Granqvist, “Spectroscopic Ellipsometry Characterization of Electrochromic Tungsten Oxide and Nickel Oxide Thin Films Made by Sputter Deposition,” *Solar Energy Materials & Solar Cells* 94 (2010) 724-733.

[13] M. A. Vidales-Hurtado and A. Mendoza-Galván, “Optical and Structural Characterization of Nickel Oxide-Based Thin Films Obtained by Chemical Bath Deposition,” *Materials Chemistry and Physics* 107(2008) 33-38.

[14] E. OzkanZayim, I. Turhan, F.Z. Tepehan and N. Ozer,“Sol-Gel Deposited Nickel Oxide Films for Electrochromic Applications,” *Solar Energy Materials & Solar Cells* 92 (2008) 164-196.

[15] S. A. Mahmoud, ShereenAlshomer, Mou’ad A. Tarawnh, “Structural and Optical Dispersion Characterisation of Sprayed Nickel Oxide Thin Films”, *Journal of Modern Physics* 2 (2011) 1178-1186.

[16] A. Arshak, S. Zleetni, K. Arshak, “Sensor “,2(2002) 174.

[17] A. Hagfeldt, M. Gratzel, *Chem. Rev.* 95 (1995) 49.

[18] M. Janai, D.D. Alfred, D.C. Booth and B.O. Seraphin, *Sol. Ener. Mater.* 1(1979) 11.

[19] K. L. Chopra, Thin Film Phenomena, McGraw Hill Book Company USA (1983) 729.

[20] M. Hanson, "Constitution of binary alloys", Mc. Grow-Hill Book Company (1958).