Effects of Cu-doping on Optical Properties of NiO

Nidhal Nissan Jandow*
Al_Mustansiriyah University, College of Education, Physics Department, Baghdad, Iraq
*E-mail address: nidhalnissan@yahoo.com

ABSTRACT

This work presents the effect of Cu-doping on some optical properties of Cu:NiO thin film prepared by spray pyrolysis technique. UV-Visible spectrophotometer in the range 380-900 nm used to determine the absorbance spectra for various Cu-doping of Cu:NiO thin film. The transmittance and energy gap are decreased with increasing Cu-doping in the prepared films, while absorption coefficient, extinction coefficient, and skin depth are increased with increasing Cu-doping.

Keywords: chemical spray pyrolysis; optical properties; NiO thin films; energy gap

1. INTRODUCTION

Bulk NiO has a cubic rock-salt crystal structure (Fm-3m) undergoing a weak cubic-to-rhombohedral distortion (R-3m) below the Néel temperature $T_N=523$ K due to the magnetostriction effect [1]. The composition of nickel oxide can be represented as NiO$_x$H$_y$ but for simplicity, it is referred to as NiO$_x$ [2]. They are attractive materials which have lots of special properties such as optical, electrical and magnetic properties. They have been employed as an antiferramagnetic material [3], p-type transparent conducting films [4], a material for electro chromic display devices [5] and a part of functional sensor layers in chemical sensors [6].

Several methods can be used to prepare NiO thin film such as sol-gel [7], spray pyrolysis [8], plasma enhanced chemical vapor deposition [9], pulsed laser deposition [10-11] and magnetron sputtering [12-15]. Among various methods, spray pyrolysis is one through which the films can be coated for large area.

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

2. EXPERIMENTAL DETAILS

Dissolved nickel chloride hexahydrate (NiCl$_2$.6H$_2$O) (from sigma-Aldrich company) with re-distilled water was used as a starting solution for deposition thin films of Cu:NiO by using chemical spray pyrolysis method. The dissolve solution was made with $100$ ml of redistilled water to make $0.1$ M solution. The volumetric ratio of Cu was $2\%$ and $4\%$ and substrate temperature was $380\, ^\circ C$. 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 3ml/min, 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) were maintained at a pressure of $10^{-5}$ Nm$^{-2}$.

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

3. RESULTS AND DISCUSSION

The optical properties of the deposited Cu : NiO thin films on glass substrate temperature 380 ºC with various contain of Cu by using UV-Visible spectrophotometer in the region of 380-900 nm. Fig.1 represent the relationship between transmittance and wavelength of Cu : NiO thin films. From this figure, it can notice that the transmittance decreased with increasing contain of Cu in NiO thin films, this may be attributed to the creation of levels at the energy band by increasing Cu contain.

![Fig. 1. The relationship between transmittance spectra and wavelength for Cu:NiO thin film.](image)

Fig. 2 represent absorption coefficient behavior of various photon energy of NiO thin film with various contain of Cu. From this figure, it can notice the absorption coefficient increases with increasing photon energy for all prepared films, and increases with increasing Cu contain.
From Tauc equation, the relation between $\alpha h\nu$ and photon energy ($h\nu$) was examined for different values of $r$ to determine the type of the optical transition. The best fit line can be chosen where the value of $r$ equal to $1/2$ which represents an allowed direct transition [16]. The straight line portion in the strong absorption region is extrapolated at $\alpha h\nu = 0$ and the value obtained represents the optical energy gap as shown in Figs 3-5. From these figures it can notice that the energy gap are decreased from 3.1 eV for pure NiO thin film to 2.9 eV after 4% added of Cu for NiO thin film.
Fig. 4. $(\alpha h\nu)^2$ versus $h\nu$ for 2% Cu-doped NiO thin film.

Fig. 5. $(\alpha h\nu)^2$ versus $h\nu$ for 4% Cu-doped NiO thin film.
The extinction coefficient \( (k) \), which is related to the exponential decay of the wave as it passes through the medium, is defined as \([17]\):\[
\frac{\alpha \lambda}{4\pi} = k
\] (1)

where \( \alpha \) is the absorption coefficient and \( \lambda \) is the wavelength. Fig. 6 represent the relationship between extinction coefficient and wavelength. From this figure, it can notice the increases of \( k \) with increasing content of Cu in the Cu : NiO thin film.

![Graph showing extinction coefficient vs. wavelength for different Cu:NiO thin film compositions.](image)

**Fig. 6.** The relationship between extinction coefficient and wavelength for Cu:NiO thin film.

The refractive index \( (n) \) has been found by using the relation \([18]\):\[
R = \frac{(n - 1)^2}{(n + 1)^2}
\] (2)

Fig. 7 represent the relationship between the refractive index and the wavelength. From this figure, it can notice the unstable behavior of refractive index that depend on wavelength.
Fig. 7. The relationship between refractive index and wavelength for Cu:NiO thin film.

The skin depth ($\chi$) represents the electromagnetic wave will have amplitude reduced after traversing a thickness that calculated from the following relation [19]:

$$\chi = \frac{1}{\alpha}$$

(4)

Fig. 8 showing the variation of skin depth with wavelength. Skin depth increased with increasing Cu contain in Cu : NiO thin film.

Fig. 8. The relationship between skin depth and wavelength for Cu:NiO thin film.
4. CONCLUSION

The effect of Cu-doping on some optical properties of Cu : NiO thin film prepared by spray pyrolysis technique is studied. The transmittance is decreased with increasing Cu-doping in the prepared films, while absorption coefficient, extinction coefficient, and skin depth are increased with increasing Cu-doping. Energy gap decreased from 3.1 eV for a pure NiO thin film to 2.9 eV after 4% addition of Cu for NiO thin film.

References

[1] W. L. Roth, Phys. Rev. 110 (1958) 1333.
[2] A. Kuzmin, J. Purans, and A. Rodionov, J. Phys: Condens. Mater. 9(1997)6979.
[3] E. Fujii, A. Tomozawa, H. Torii, R. Takayama, Jpn. J. Appl. Phys. 35(1996)L328.
[4] H. Sato, T. Minami, S. Takata, T. Yamada, Thin Solid Films 236(1993)27.
[5] K. Youshmura, T. Miki, S. Tanemura, Jpn. J. Appl. Phys. 34(1995)2440.
[6] H. Kumagai, M. Matsumoto, K. Toyoda, M. Obara, J. Mater. Sci. 15(1996)1081.
[7] Y. R. Park, K. J. Kim, “Solgel preparation and optical characterization of NiO and Ni1−xZnxO thin films”, Journal of Crystal Growth 258 (2003) 380–384.
[8] B. A. Reguig, A. Khelil, L. Cattin, M. Morsli and J.C. Bernede, “Properties of NiO thin films deposited by intermittent spray pyrolysis process”, Applied Surface Science 253 (2007) 4330–4334.
[9] W. C. Yeh and M. Matsumura, “Chemical vapor deposition of nickel oxide films from bis-π-cyclopentadienyl-nickel”, Jpn. J. Appl. Phys. 36(1997) 6884–6887.
[10] U. S. Joshi, R. Takahashi, Y. Matsumoto, H. Koinuma, “Structure of NiO and Li-doped NiO single crystalline thin layers with atomically flat surface”, Thin Solid Films 486 (2005) 214–217.
[11] Y. Kakehi, S. Nakao, K. Satoh, T. Kusaka, “Room-temperature epitaxial growth of NiO(111) thin films by pulsed laser deposition”, Journal of Crystal Growth 237-239 (2002) 591–595.
[12] H. L. Chen, Y.M. Lu, W.S. Hwang, “Thickness dependence of electrical and optical properties of sputtered nickel oxide films”, Thin Solid Films 498(2006) 266–270.
[13] Ying Zhou, Donghong Gu, Yongyou Geng, Fuxi Gan, “Thermal, structural and optical properties of NiOx thin films deposited by reactive dc-magnetron sputtering”, Materials Science and Engineering B135 (2006) 125–128.
[14] Y. M. Lu, W.S. Hwang, J.S. Yang, H.C. Chuang, “Properties of nickel oxide thin films deposited by RF reactive magnetron sputtering”, Thin Solid Films 420-421 (2002) 54–61.
[15] H. L. Chen, Y.M. Lu, W.S. Hwang, “Characterization of sputtered NiO thin films”, Surface and Coatings Technology 198 (2005) 138–142.
[16] J. Tauc, Amorphous and Liquid Semiconductors, London (1974).
[17] R. A. Grenier, "Semiconductor Device", Electronic Energy Series, McGraw-Hill, Book Co. Inc. (1961).

[18] Ludmila Ekertova, Physics of Thin Films, (1977).

[19] J. F. Eloy, "Power Lasers", National School of Physics, Grenoble, France, John Wiley & Sons (1984) 59.

(Received 01 March 2015; accepted 18 March 2015)