



RESEARCH ARTICLE

Investigation of Optical Properties of NiO_{0.99}Cu_{0.01} Thin Film by Thermal Evaporation Technique

* **Sudad S.Ahmed , Eman K.Hassan, Ghuson H.Mohamed**
Physics Department, College of Science, University of Baghdad/ Iraq

Manuscript Info

Manuscript History:

Received: 12 December 2013
Final Accepted: 22 January 2014
Published Online: February 2014

Key words:

Optical properties; NiO:Cu;
Thermal evaporation; energy gap.

*Corresponding Author

Sudad S.Ahmed

Abstract

In this paper, NiO_{0.99}Cu_{0.01} thin films were deposited by using thermal evaporation technique on Si substrates under vacuum 10⁻⁵ mbar. The structure and crystallite size of these films were established using atomic force microscope (AFM) and x-ray diffraction (XRD), it shows that the structure is polycrystalline and the average diameter is around 97.21nm. The optical properties; absorption, transmission, and reflection, as functions of wavelength were measured. Optical constants such as (refractive index n, dielectric constants $\epsilon_{i,r}$ and extinction coefficient k) of the deposition films were obtained from the analysis of the experimental recorded transmittance spectral data. The optical band gap of NiO_{0.99}Cu_{0.01} films are calculate from $(\alpha h\nu)^{1/2}$ vs. photon energy curve and from photoluminescence spectra.

Copy Right, IJAR, 2013., All rights reserv

1.Introduction

Transparent Conducting Oxides (TCO) thin films like Nickel Oxide are attracting more attention because they are important in several scientific and technological applications. They have been employed as an antiferromagnetic material^[1], p-type transparent conducting films^[2], electro catalysis^[3], positive electrode in batteries^[4], fuel cell^[5], a material for electro-chromic display devices^[6], part of functional sensor layers in chemical sensors^[7], solar thermal absorber^[8], catalyst for oxygen evolution^[9], and photo electrolysis^[10].

NiO films have been fabricated by a number of techniques including sol-gel^[11], spray pyrolysis^[12], plasma enhanced chemical vapor deposition^[13], pulsed laser deposition^[14,15], and magnetron sputtering^[16-19]. The present paper reports fabrication of NiO_{0.99}Cu_{0.01} thin films by thermal evaporation technique in order to study the optical constants of the NiO doped Cu thin films.

2. EXPERIMENTAL WORK

NiO doped Cu thin films were prepared by using thermal evaporation technique onto p-type Si substrate under vacuum 10⁻⁵ mbar by the combination of rotary and diffusion pump. The NiO powder was doped with (0.01 wt %) of Cu (99.99% purity). The thickness of the films was 500nm.

The structure of the films was obtained using x-ray diffraction (XRD) (Shimadzo 6-2006, with Cu-K α radiation having wavelength $\lambda= 1.5406 \text{ \AA}$). Microstructure surface topography was estimated using (AFM).

Optical transmittance was recorded with a double beam Shimadzu UV-Visible spectrophotometer in the wavelength rang 200-900 nm.

3. RESULTS AND DESCUSSION

The XRD pattern of NiO_{0.99}Cu_{0.01} thin film was shown in Fig.(1). The analysis of structure of deposited NiO_{0.99}Cu_{0.01} films were polycrystalline with two weak diffraction peaks appeared at about the position of 37.12^o and 43.3^o with the preferential orientation (111),(200) respectively. Although there are other peaks, which are within the noise level. The XRD pattern of the NiO_{0.99}Cu_{0.01} only appear NiO peaks, this was confirmed by chen et.al^[20].

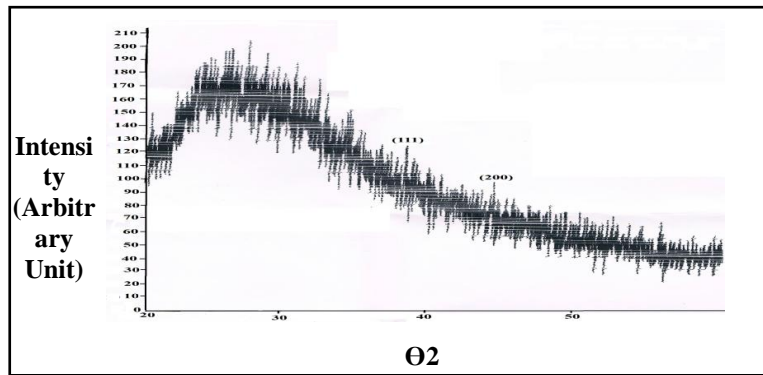


Fig.(1) X-ray diffraction of NiO_{0.99}Cu_{0.01} thin films on Si substrate.

AFM images (2D&3D) were prepared of the NiO_{0.99}Cu_{0.01} thin films on Si substrates as shown in Fig.(2). This Fig. shows the Roughness average is about 0.596 nm and the Root Mean Square about 0.706 nm. Fig.(3) shows the grain analysis report which estimated for the NiO_{0.99}Cu_{0.01} thin films and the average diameter of the particles about 97.21 nm.

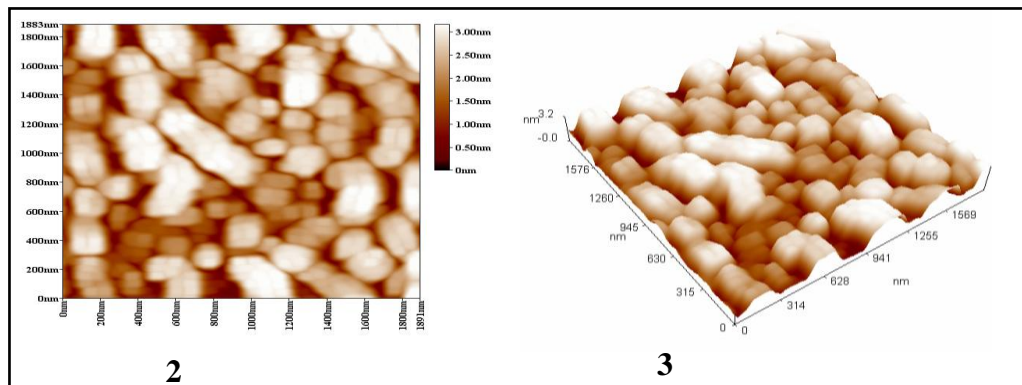


Fig.(2) AFM images (2D& 3D) of NiO_{0.99}Cu_{0.01} thin films.

NiO_{0.99}Cu_{0.01} thin films recorded in the range 200-900 nm. Fig.(4) shows the Transmission & the Absorption vs. wavelength spectrum of NiO_{0.99}Cu_{0.01} thin films of thickness 500 nm. It can be seen that the NiO_{0.99}Cu_{0.01} thin films having a high transparency in the VIS-IR regions, while the transparency in the UV region was very low. The spectrum of absorption were also estimated as shown in Fig.(4). It is opposite to that of transmittance spectrum.

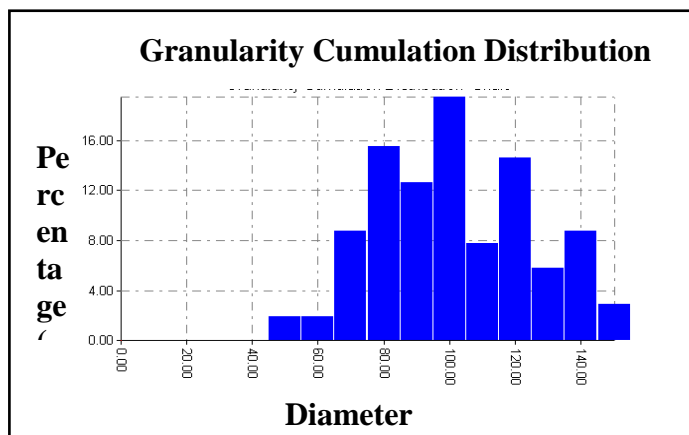


Fig.(3) AFM grain analysis report for the NiO_{0.99}Cu_{0.01} film of 500 nm thickness.

The reflectance (R) has been found by using the relationship:

$$R+T+A=1 \dots\dots\dots (1)$$

Where (A) is the absorption & (T) is the transmission. Fig.(5) shows the reflectance spectra for the NiO_{0.99}Cu_{0.01} thin films as a function of wavelength. It is clear from this figure that the reflectance of the films increased with the increasing of the wavelength.

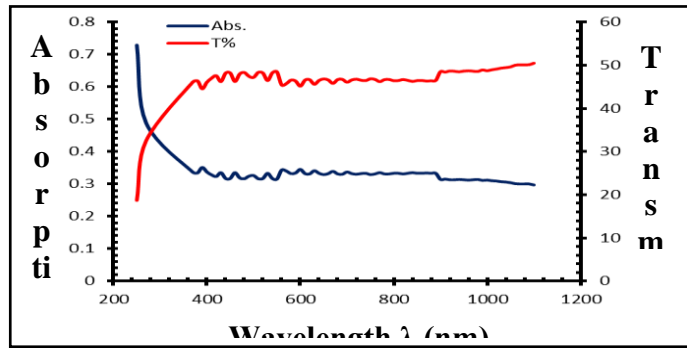


Fig.(4) Transmission & Absorption spectrum as a function of wavelength for NiO_{0.99}Cu_{0.01} thin film

The absorption coefficient (α) could be calculated by using the following relation^[21]:

$$\alpha = \frac{2.303 A}{t} \dots\dots\dots (2)$$

Where (t) is the film thickness.

Fig.(6) shows the dependence of the absorption coefficient(α) on the wavelength. This figure shows that, the absorption coefficient (α) decreases with the increasing of wavelength and the cut off wavelength ($\lambda_{\text{cut off}}$) around 620 nm.

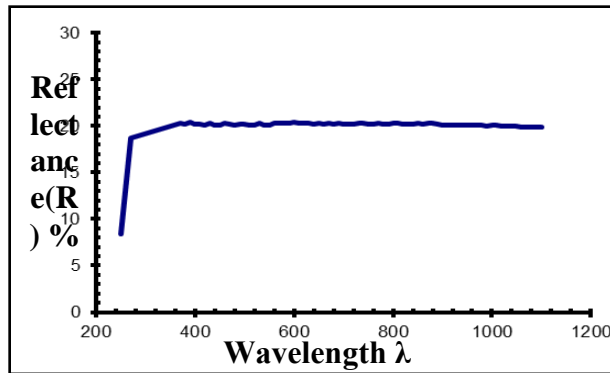


Fig.(5) Reflectance as a function of wavelength for NiO_{0.99}Cu_{0.01} thin films.

The value of the band gap (E_g) of NiO_{0.99}Cu_{0.01} can be deduced from the plot of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$), as seen in Fig.(7).

From Fig.(7), it is observed that there exists a linear dependence of $(\alpha h\nu)^2$ with $h\nu$ in the high photon energy region. Extrapolation of the linear portion to the $h\nu$ axis would yield the band gap (E_g) of the film. From this figure, it can be seen that the band gap was about 3.1 eV and this value is in good agreement with the reported value of 3.15-4.0 eV^[22].

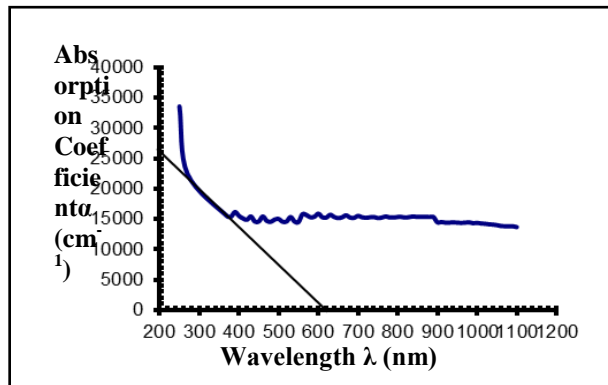


Fig.(6) Absorption Coefficient as a function of wavelength for NiO_{0.99}Cu_{0.01} thin film

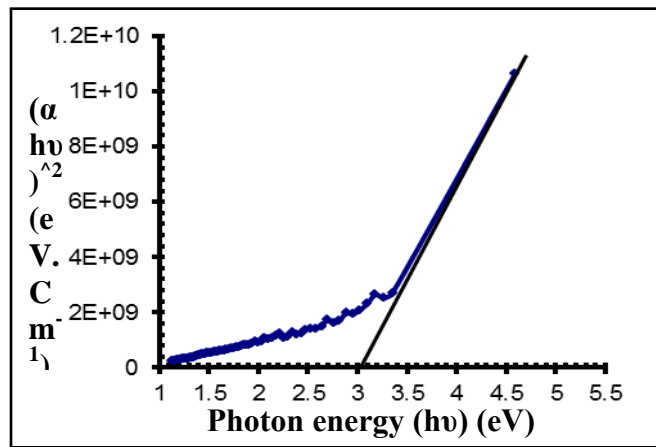


Fig.(7) $(\alpha h\nu)^2$ as a function of Photon energy $(h\nu)$ for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin films.

The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation^[23]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \dots\dots\dots (3)$$

Where k is the extinction coefficient ($k=\alpha\lambda/4\pi$).

Fig.(8) shows the variation of the refractive index as a function of the wavelength for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin films, which indicate that the refractive index increases with increasing of wavelength.

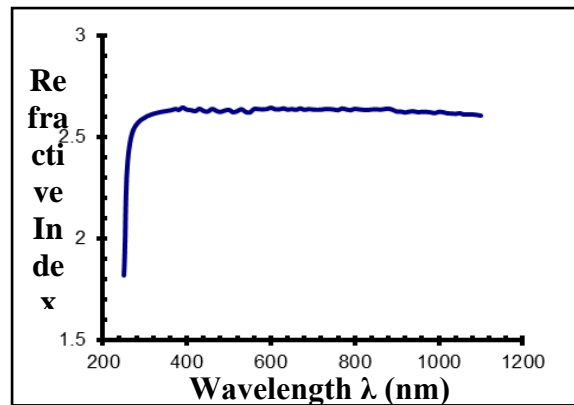


Fig.(8) Refractive Index as a function of wavelength for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin

The relation between the extinction coefficient (k) and wavelength for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ films deposited are shown in Fig.(9). From this figure we can observe that k increases with increasing of wavelength.

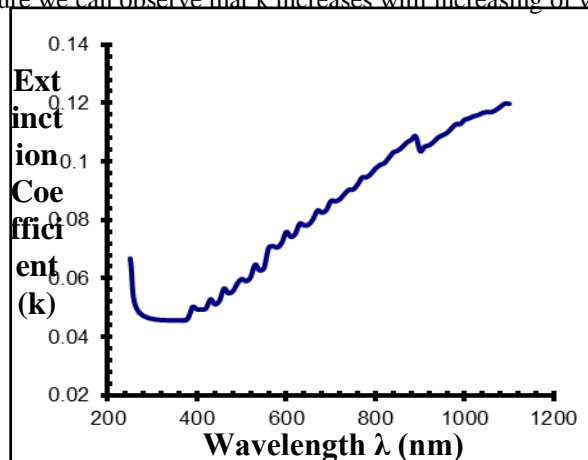


Fig.(9) Extinction Coefficient (k) as a function of wavelength for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin films.

The dielectric constant is defined as $\epsilon(\omega) = \epsilon_r(\omega) + i\epsilon_i(\omega)$, real and imaginary parts of the dielectric constant are related to the n and k values. The ϵ_r and ϵ_i values were calculated using the formulas^[24]:

$$\epsilon_r = n^2 - k^2 \dots\dots\dots (4) \quad \epsilon_i = 2nk \dots\dots\dots (5)$$

The variation of the real (ϵ_r) and imaginary (ϵ_i) parts of the dielectric constant values versus wavelength in the range 200-1200 nm are shown in Fig.(10).

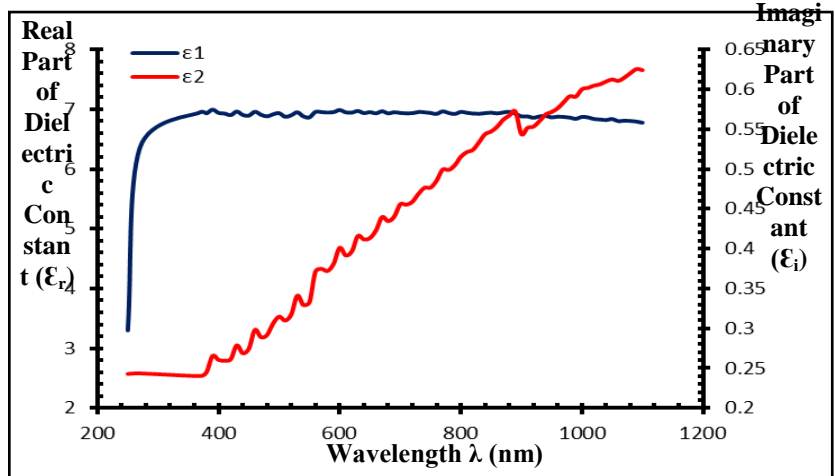


Fig.(10) Variation of ϵ_r & ϵ_i as a function of wavelength for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin films.

From Fig.(10) we can observe that real parts of the dielectric constant increase as the wavelength increase. Also the variation of (ϵ_r) has similar trend to the variation of the refractive index because of the smaller values of k^2 in comparison with n^2 and the values of real part are higher than imaginary part. The imaginary part of the dielectric constant as shown in Fig.(10). The variation of the (ϵ_i) mainly depends on the variation of k values which related to the variation of absorption coefficient.

The photoluminescence spectrum (PL) of $\text{NiO}_{0.99}\text{Cu}_{0.01}$ film excited by 320 nm line is shown in Fig.(11).

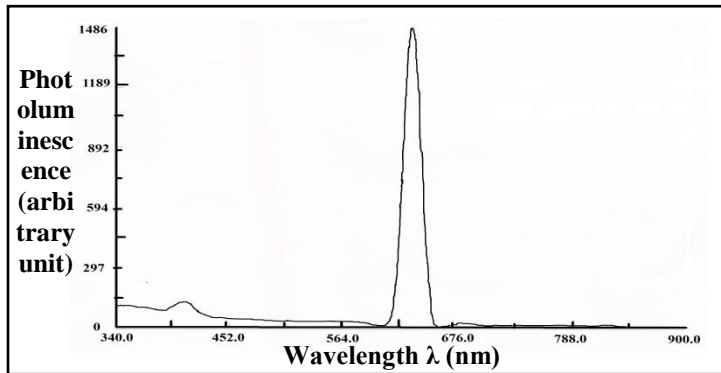


Fig.(11) The Photoluminescence spectrum (PL) for $\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin films.

The spectrum shows two peaks: the first peak at 404 nm which can be referred to the direct band transition. The second peak at 620 nm is due to the exciton emission. The intensity at the 620 nm peak is higher than that found around 404 nm peak. This is because the direct band transition quenched by the defect states.

The energy band gap from photoluminescence spectrum of the $\text{NiO}_{0.99}\text{Cu}_{0.01}$ film is calculated by using the following equation:

$$E_g = \frac{1240}{\lambda(\text{nm})} \dots\dots\dots (6)$$

For the PL wavelength 404 nm the energy band gap is found to be 3.07 eV.

4. CONCLUSION

$\text{NiO}_{0.99}\text{Cu}_{0.01}$ thin films were prepared using thermal evaporation technique onto Si substrate under vacuum equal to 10^{-5} mbar. The thickness of the films was 500 nm. The structure analysis shows that the films are polycrystalline structure. From UV-VIS transmittance, absorbance spectra, it observed that the optical transition in

the NiO_{0.99}Cu_{0.01} films to be direct transition. The energy band gap calculated from PL spectrum and found equal to 3.07 eV.

REFERENCES

1. E. Fujii, A. Tomozawa, H. Torii, R. Takayama, " Preferred Orientations of NiO Films Prepared by Plasma-Enhanced Metalorganic Chemical Vapor Deposition" *Jpn. J. Appl. Phys.* 35 (1996) L328-L330.
2. H. Sato, T. Minami, S. Takata, T. Yamada, " Transparent conducting p-type NiO thin films prepared by magnetron sputtering", *Thin Solid Films*, Vol. 236 (1993) 27-31.
3. E. J. M. O'Sullivan and E. J. Calvo, "Reactions at Metal Oxide Electrodes *Comprehensive Chemical Kinetics*" Elsevier, New York, 1987.
4. C. M. Lambert and G. Nazri, P. C. Yu, "Spectroscopic and Electrochemical Studies of Electrochromic Hydrated Nickel Oxide Films", *Solar Energy Materials*, Vol. 16 (1987) 1-17. doi:10.1016/0165-1633(87)90003-7.
5. N. Shaigan, D.G. Ivey and W. Chen, "Metal-Oxide Scale Interfacial Imperfections and Performance of Stainless Steels Utilized as Interconnects in Solid Oxide Fuel Cells", *Journal of The Electrochemical Society*, Vol. 156 (2009) B765-B770.
6. K.K. Purushothaman and G. Muralidharan, "Nanostructured NiO Based All Solid State Electrochromic Device", *Journal of Sol-Gel Science and Technology*, Vol. 46 (2008) 190-197. doi:10.1007/s10971-007-1657-0 .
7. I. Hotovy, J. Huran, L. Spiess, S. Hascik, V. Rehacek, " Preparation of nickel oxide thin films for gas sensors applications", *Sensors and Actuators B: Chemical*, Vol. 57(1999) 147-152.
8. R. Cerc Korosec, P. Bukovec, B. Pihlar, A. Surca Vuk, B. Orel and G. Drazic, " Preparation and Structural Investigations of Electrochromic Nanosized NiOx Films Made via the Sol-Gel Route", *Solid State Ionics*, Vol. 165 (2003) 191-200. doi:10.1016/j.ssi.2003.08.032 .
9. B. Sasi and K. G. Gopalchandran, "Nanostructured Mesoporous Nickel Oxide Thin Films", *Nanotechnology*, Vol. 18 (2007) 115613-115617.
10. H. Kamel, E. K. Elmaghraby, S. A. Ali and K. Abdel-Hady, " The Electrochromic Behavior of Nickel Oxide Films Sprayed at Different Preparative Conditions", *Thin Solid Films*, Vol. 483(2005) 330-339. doi:10.1016/j.tsf.2004.12.022.
11. Y.R. Park, K.J. Kim, "Sol gel preparation and optical characterization of NiO and Ni_{1-x}Zn_xO thin films", *Journal of Crystal Growth*, Vol.258, No.3-4, pp.380-384, 2003.
12. B.A. Reguig, A. Khelil, L. Cattin, M. Morsli and J.C. Bernède, "Properties of NiO thin films deposited by intermittent spray pyrolysis process", *Applied Surface Science*, Vol.253, No.9, pp.4330-4334, 2007.
13. W.C. Yeh and M. Matsumura, "Chemical vapor deposition of nickel oxide films from bis- π -cyclopentadienyl-nickel", *Jpn. J. Appl. Phys.*, Vol.36 Part 1, No.11, pp.6884-6887, 1997.
14. 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*, Vol.486, No.1-2, pp.214-217, 2005.
15. 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*, Vol.237-239, No.1, pp.591-595, 2002.
16. H.L. Chen, Y.M. Lu, W.S. Hwang, "Thickness dependence of electrical and optical properties of sputtered nickel oxide films", *Thin Solid Films*, Vol.498, No.1-2, pp.266-270, 2006.
17. 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 B*, Vol.135, No.2, pp.125-128, 2006.
18. 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*, Vol.420-421, pp.54-61, 2002.
19. H.L. Chen, Y.M. Lu, W.S. Hwang, "Characterization of sputtered NiO thin films", *Surface and Coatings Technology*, Vol.198, No.1-3, pp.138-142, 2005.
20. S. C. Chen, T. Y. Kuo, Y. C. Lin, and C. L. Chang, "Preparation and properties of p-type transparent conductive NiO films", *Adv. Mater. Res.* Vol. 123-125 (2010) 181-184.
21. Han, X., Liu, R., Chen, W. and Xu, Z, " Properties of nanocrystalline zinc oxide thin films prepared by thermal decomposition of electrodeposited zinc peroxide", *Thin Solid Films*, Vol. 516 (2008) 4025- 4029.
22. H. Sato, T. Minami, S. Takata, T. Yamada, "Transparent conducting p-Type NiO thin-films prepared by magnetron sputtering", *Thin Solid Films*, Vol.236, No.1-2, pp.27-31, 1993.
23. N.A. Subrahmanyam, "A textbook of Optics", Brj Laboratory, Delhi, 1977.
24. T.S. Moss, G.J. Burrell, B. Ellis, "Semiconductor Opto-Electronics", Wiley, New York, 1973.