The effect of annealing temperatures on the optical parameters of $NiO_{0.99}Cu_{0.01}$ thin films

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Abstract

$NiO_{0.99}Cu_{0.01}$ films have been deposited using thermal evaporation technique on glass substrates under vacuum 10^{-5}mbar. The thickness of the films was 220nm. The as -deposited films were annealed to different annealing temperatures (373, 423, and 473) K under vacuum 10^{-3}mbar for 1 h. The structural properties of the films were examined using X-ray diffraction (XRD). The results show that no clear diffraction peaks in the range 2θ= $(20\text{-}50)^o$ for the as deposited films. On the other hand, by annealing the films to 423K in vacuum for 1 h, a weak reflection peak attributable to cubic NiO was detected. On heating the films at 473K for 1 h, this peak was observed to be stronger. The most intense peak is at 2θ = 37.12^o with the preferential orientation of the films being (111) plane. The optical properties of the films have been studied. The effect of annealing temperature on the optical parameters of $NiO_{0.99}Cu_{0.01}$ such as transmittance, reflectance, absorption coefficient, refractive index, extinction coefficient, and real and imaginary parts of dielectric constant has been reported.

Key words

Optical properties, Nickel Oxide films, NiO:Cu, structural properties.

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تأثير درجة حرارة التلدين على المعلمات البصرية لأغشية $NiO_{0.99}Cu_{0.01}$ الرقيقه

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الخلاصة

تم ترسيب أغشيه رقيقه من أوكسيد النيكل المشوب بالنحاس $NiO_{0.99}:Cu_{0.01}$ على قواعد زجاجية باستخدام تقنية التبخير الحراري. تم دراسة الخواص البصرية للاغشية المحضرة كداله لدرجة حرارة التلدين. تم تلدين الاغشية المحضرة لثلاث درجات حرارة تلدين (373، 423، و 473) كلفن. تم فحص خصائص تركيب الاغشية المحضرة باستخدام حيود الاشعة السينية (XRD). لقد اظهر فحص تركيب هذه الاغشية بانه لاتوجد اي قمم ضمن المدى $(20\text{-}50)^o$ 2θ للغشاء المحضر في درجة حرارة الغرفة، بينما عند تلدين الاغشية لدرجة حرارة 423K ولمدة ساعة واحدة ظهرت قمة ضعيفة، وبزيادة درجة حرارة التلدين الى 473K ظهر بان القمة اصبحت اكثر شدة وان الأتجاهات الشبيكية المفضلة لبلورات الغشاء هي(111). تم دراسة تأثير التلدين على المعلمات البصرية لأغشية $NiO_{0.99}:Cu_{0.01}$ الرقيقة مثل: النفاذية، الانعكاسية، معامل الامتصاص، معامل الأنكسار، معامل الخمود، ثابت العزل الحقيقي وثابت العزل الخيالي.

Introduction

Transition metal oxides like Nickel oxide are an attractive material which has lots of special properties such as optical, electrical and magnetic properties. It offers promising candidature for many applications, They have been employed as an antiferramagnetic 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 can be prepared by multiple physical and chemical methods such as: spray pyrolysis [11,12], electron beam evaporation [13] pulsed laser deposition [14], chemical bath deposition [15] and sol-gel [16], plasma-enhanced chemical vapor deposition [17] and sputtering [18] have been used to obtain nickel oxide films. All these methods offer different advantages depending on the application of interest and many efforts have been conduced to obtain films with the desirable physical and/or chemical properties. In the case of wide-band-gap semiconductors, addition of impurities often induced dramatic change in their optical and electrical properties. It is well known that the physical characteristics of the NiO films depend on the doping, and then a study of the doping effect on the physical characteristics is always interesting. In the present investigation we report the effect of annealing on $NiO_{0.99}Cu_{0.01}$ thin films prepared by thermal evaporation technique in order to study the optical constants, including refractive index, extinction coefficient, real and imaginary part of dielectric constant.

Experimental details

1. NiO:Cu nanoparticles growth

During this work Cu doped NiO thin films were prepared using thermal evaporation technique onto glass substrates under vacuum 10^{-5} mbar by the combination of rotary and diffusion pump. The NiO powder was doped with (0.01wt%) of Cu (99.99% purity). The thickness of films was 220nm. The annealing process was continued for 1 hour was to improve the properties of the films. The glass slides substrate of 3 x 2 cm^2 area were cleaned with dislated water using ultrasonic process for 15 minute to deposit the films.

2. Characterization of thin films

X-ray diffraction (XRD) pattern was used to determine the structural properties of NiO:Cu using CuKα radiation of wavelength 1.54Å, the current was 20 mA, the voltage was 30 kV, and the scanning angle 2θ was varied in the range of (20–50) degree with speed of 2 $cm.min^{-1}$.
The optical transmittance was recorded with a double beam Shimadzu UV - visible spectrophotometer in the wavelength range 300–800 nm. In this work the main parameter that control the properties of the films are the annealing temperatures (373, 423, and 473)K. The effect of annealing temperatures on the optical constants was examined.

Results and discussion

The XRD pattern and the values related to peaks for $NiO_{0.99}$:$Cu_{0.01}$ thin films are shown in Fig.1. As deposited $NiO_{0.99}Cu_{0.01}$ films were amorphous. After heating the films to 373K the XRD patterns shows no clear diffraction peaks in the range 2θ $(20\text{-}50)^o$. On the other hand, increasing the annealing temperature to 423K in vacuum for one hour, a weak reflection peak attributable to cubic NiO was detected. This peak was observed to be stronger when heating the films to 473K for 1 h. The most intense peak is at 2θ = 37.12^o with the preferential orientation of the films being (111) plane. For film annealed to 473K there are two obvious peaks which are at 2θ=24.61^o and 37.12^o 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. [19].The diffraction peaks arising from NiO appear at 2θ= 36.98°, 37.17° and 43.34, which are values reported for cubic NiO [20,22]. These indicates that at 423K and 473K is the coexistence of β-Ni $(OH)_2$ and NiO phases. The diffraction peaks were higher than the peaks that were annealed at lower temperature, implying the high orientation and well crystalline [23]. This suggests that these films were apparently amorphous phase and that annealing induced phase transformation changes and crystallization as also confirmed by [24].

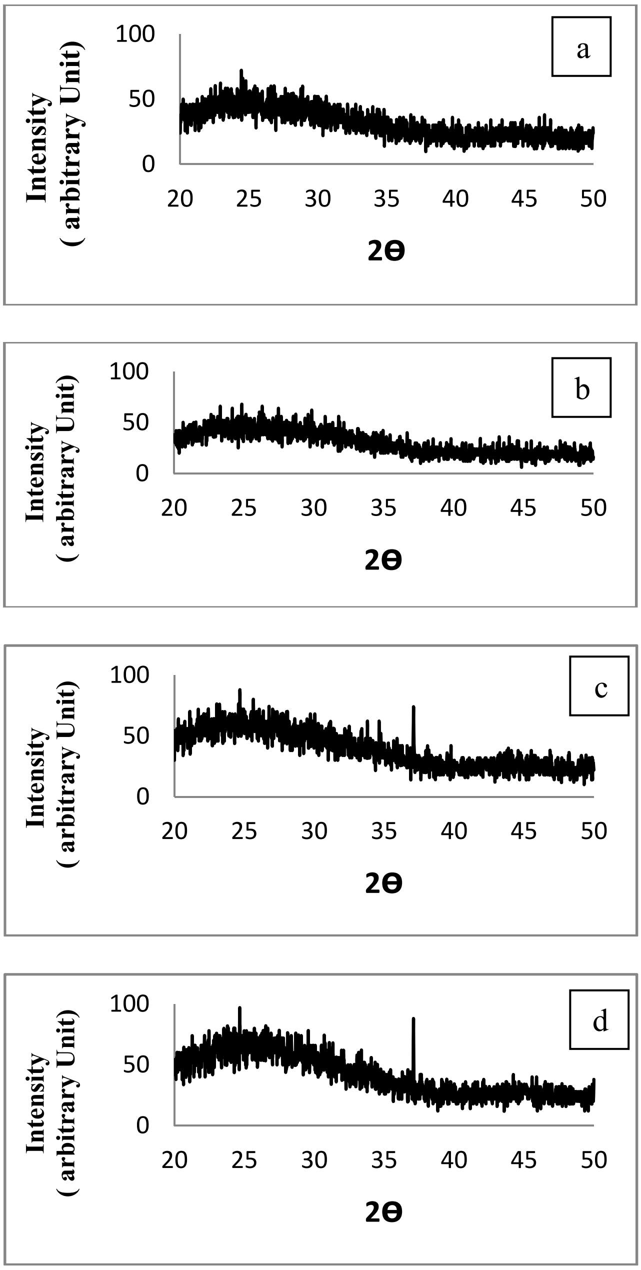

Fig. 1: XRD pattern of $NiO_{0.99}Cu_{0.01}$ thin films with different annealing temperatures (a):as deposited(303K) (b):T=RT (c):T_a=423K (d):T_a=473K

The transmission spectra of $NiO_{0.99}Cu_{0.01}$ films prepared at RT and annealed to 373, 423 and 473K is displayed in Fig. 2. From the transmission spectra it is observed that the film samples absorb heavily within

UV-VIS regions but moderately in the NIR regions for the film deposited at room temperature. The maximum absorbance for the films occurred within the UV region from where the absorbance decreased with the wavelength towards the NIR region.
The as-deposited film showed transmittance of more than 65% within the VIS-NIR regions. However both the as-deposited and annealed films show transmittance that increased exponentially from the UV region towards the NIR region. The properties of poor transmittance in the UV-VIS but moderately high transmittance in the VIS-NIR exhibited by film sample deposit at RT make the film good material for coating eye glasses for protection from sunburn caused by UV radiations.
It is clear from the figure that the spectral characterization has been affected by heat treatment. A maximum transparency of about 65% in the near IR region is observed for $NiO_{0.99}Cu_{0.01}$ thin films at room temperature. Below 600 nm there is a sharp fall in the transmittance of all films, which is due to the strong absorbance of the films in this region while the structure tends to be more transparent in the region above 600nm.

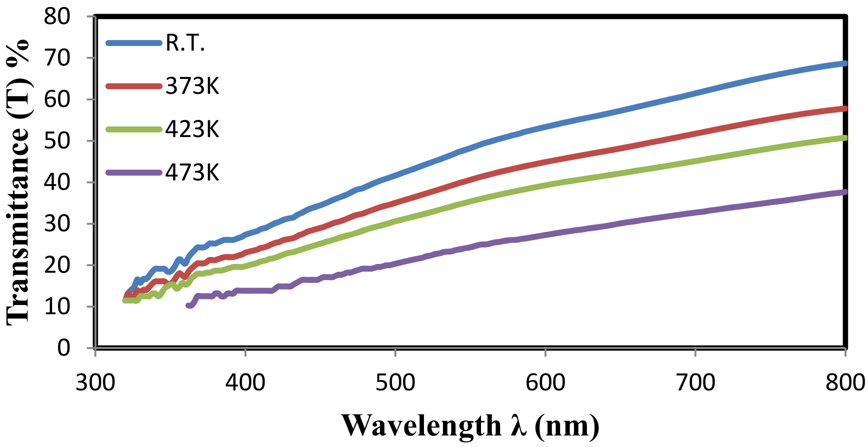

Fig. 2: The variation of transmittance spectra with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

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

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

where (A) is the absorption. Fig. 3 shows the reflectance spectra for the $NiO_{0.99}Cu_{0.01}$ thin films as a function of wavelength at different annealing temperatures. It is clear from this figure that the reflectance of the films decreased with the increasing of the annealing temperature.

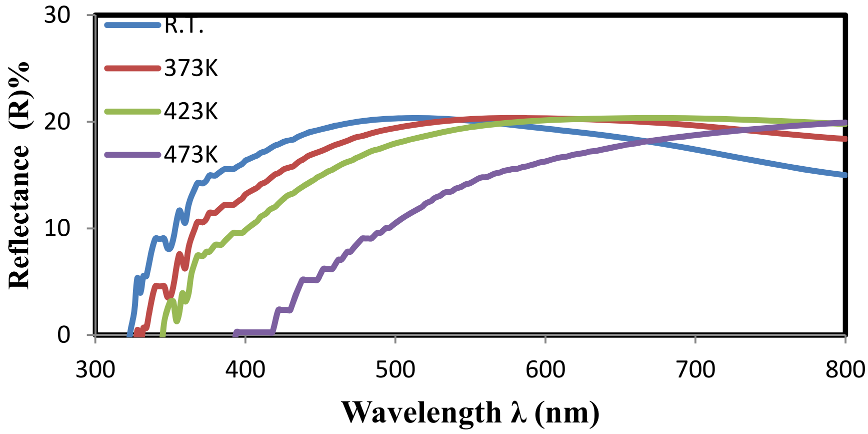

Fig. 3: The variation of reflectance spectra with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

The absorption coefficient (α) could be calculated by using the following relation [25]:

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

where t is the film thickness.

Fig. 4 shows the dependence of the absorption coefficient (α) on the wavelength for $NiO_{0.99}Cu_{0.01}$ thin films at different annealing temperatures. This figure shows that, the absorption coefficient (α) increases with the increasing of annealing temperatures. This behavior suggests that decreasing in the energy gap with increasing annealing temperature. From this figure, the absorption spectra of $NiO_{0.99}Cu_{0.01}$ films are characterized by strong absorption at higher photon energy (i.e. low wavelength) with a sharp edge on the short photon energy side. In the higher photon energy, the absorption coefficient takes higher values $>10^4 cm^{-1}$ and then it is decreased sharply with the increasing of wavelength , and beyond that the change becomes slight, this sharp or low increment is attributed to the lattice absorption bands correspond to the electronic transitions between the highest filled energy band to the lowest empty band, or also corresponds to the density of absorbing centers such as impurities absorption, excitation transition, and other defects in the crystal lattice dependent on the conditions of sample preparation.

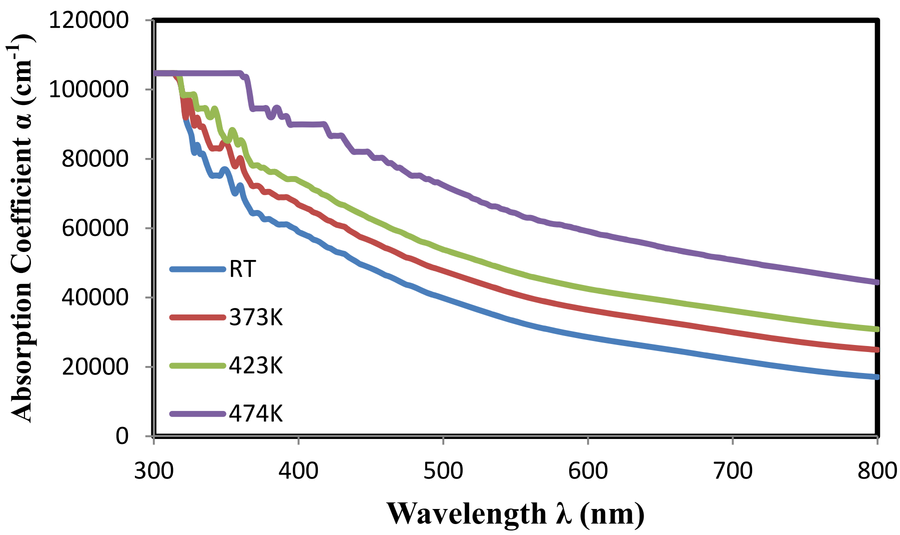

Fig. 4: The variation of absorption coefficient with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

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 [26].

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

where k is the extinction coefficient (k=αλ/4π). Fig. 5 shows the dependence of the refractive indices of $NiO_{0.99}Cu_{0.01}$ thin films on the wavelength. It can be seen that the refractive index increases with increasing of wavelength.

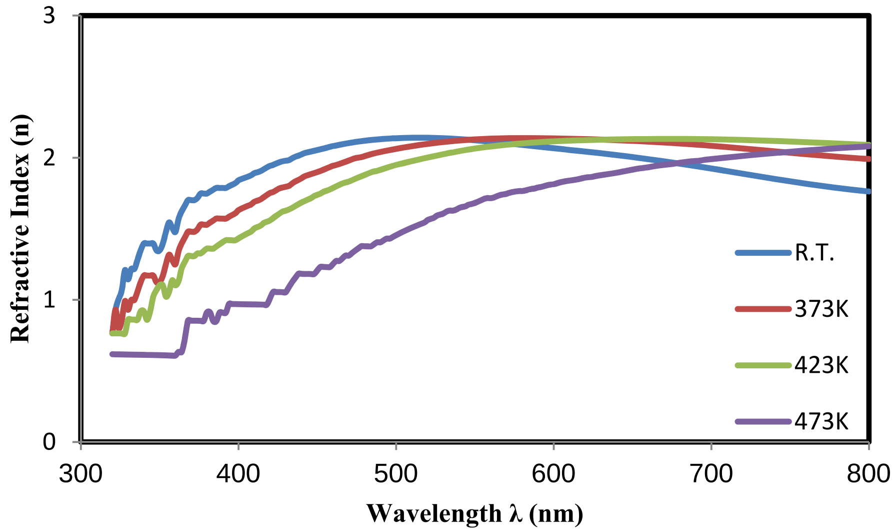

Fig. 5: The variation of refractive index with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

As it is shown in this figure that the values of the refractive increases in the range of 300-550nm and then decreases with increasing of wavelength only that was for film deposited at room temperature, the behavior increases for the annealed films at all wavelength range. Also, from this figure, it is found that the value of the refractive index decreases with the increasing of annealing temperature. This behavior may be due to the change in the bond length due to the decrease in the packing density because of increases in degree of amorphosity of films.

Fig. 6 shows the variation of extinction coefficient with the wavelength in the range of (300-800) nm. The overall extinction coefficient spectra increase with increasing annealing temperatures. It can be observed from this figure that k decreases with increasing of wavelength. This is attributed to the same reason mentioned previously in absorption coefficient.

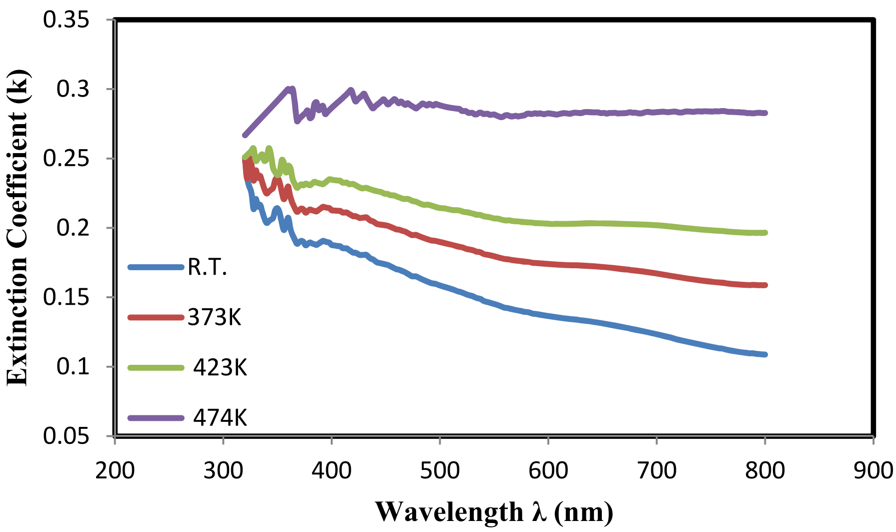

Fig. 6: The variation of extinction coefficient with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

The dielectric constant is defined as ε (ω) = εr(ω) + iεi (ω), real and imaginary parts of the dielectric constant are related to the n and k values. The εr and εi values were calculated using the formulas [27]:

$$\varepsilon_r = n^2 - k^2 \quad (4)$$

and

$$\varepsilon_i = 2nk \quad (5)$$

The variation of the real (εr) and imaginary (εi) parts of the dielectric constant values versus wavelength in the range 300-800 nm at different annealing temperatures (373, 423 and 473)K are shown in Fig. 7 and Fig. 8.

The real and imaginary parts follow the same pattern and the values of real part are higher than imaginary part. One can observe that the variation of (εr) has similar trend to the variation of the refractive index because of the smaller values of k^2 in comparison with n^2, while the variation of the (εi) mainly depend on the variation of k values which related to the variation of absorption.

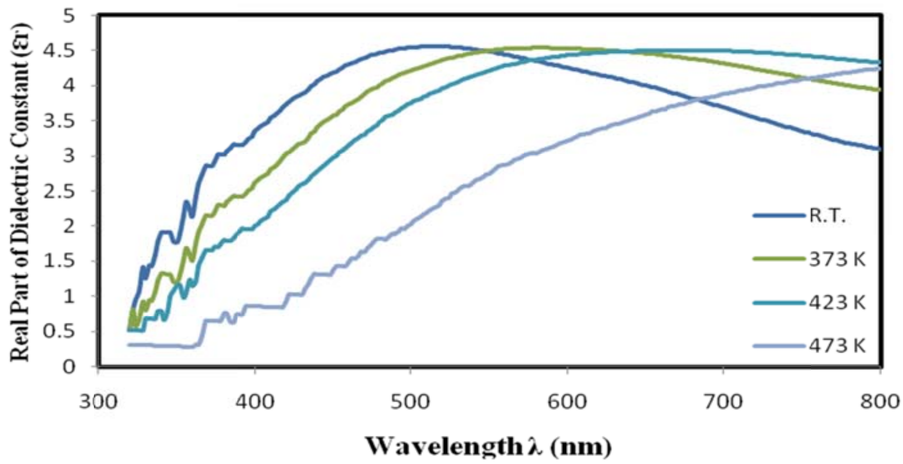

Fig. 7: The variation of εr with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

The imaginary part decreases with the increasing of wavelength except for the film annealed at 473K it is increased. It confirms the free carrier contribution to the absorption. Also, the imaginary part (εi) increases with increasing of annealing temperatures of the film, which is similar in the behavior to the variations of extinction coefficient (k) with annealing temperatures.

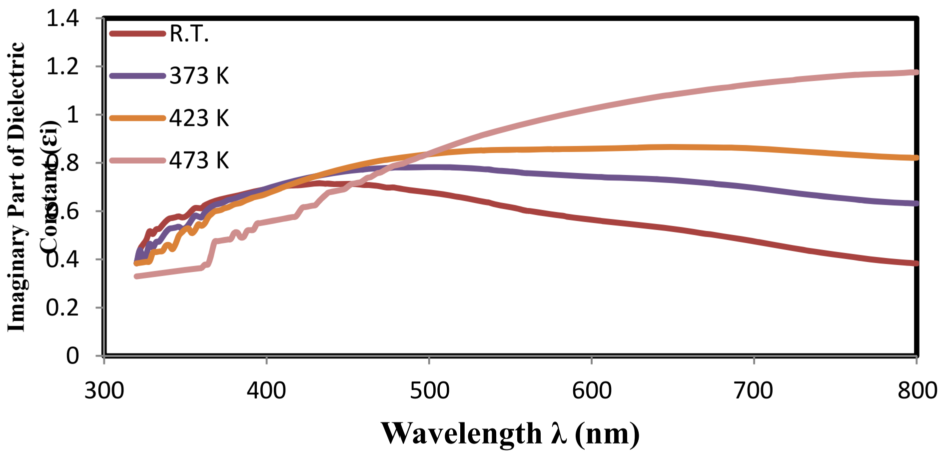

Fig. 8: The variation of εi with wavelength for $NiO_{0.99}Cu_{0.01}$ thin films.

Conclusions

$NiO_{0.99}Cu_{0.01}$ thin films were prepared by thermal evaporation technique. The structure analysis shows that the films are polycrystalline and has cubic structure. The crystalline orientation of $NiO_{0.99}Cu_{0.01}$ films being (111) and the most intense peak is at $2\theta=24.61^o$ and 37.12^o. The spectral investigations of the transmittance of $NiO_{0.99}Cu_{0.01}$ films at (300-800) nm region are affected by heat treatment and noticed that the transmission decreases with the increasing of annealing temperatures. The absorption coefficient increases with increasing of annealing temperatures and this may be attributed to the increasing in the localized state and caused a shift in absorption edge to higher wavelength. The refractive index (n), extinction coefficient (k), and dielectric constant (ε) were observed to be decrease with increasing Ta.

References

[1] E. Fujii, A. Tomozawa, H. Torii, R. Takayama, Jpn. J. Appl. Phys. 35 (1996) 328- 330.

[2] H. Sato, T. Minami, S. Takata, T. Yamada, Thin Solid Films, 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, G. Nazri, P.C.Yu, Solar Energy Materials,16 (1987) 1-17.

[5] N. Shaigan, D.G. Ivey, W. Chen, Journal of The Electrochemical Society, 156 (2009) 765- 770.

[6] K.K. Purushothaman and G. Muralidharan, Journal of Sol-Gel Science and Technology, 46 (2008) 190-197.

[7] I. Hotovy, J. Huran, L. Spiess, S. Hascik, V. Rehacek, Sensors and Actuators B: Chemical, 57(1999)147–152.

[8] R. Cerc Korosec, P. Bukovec, B. Pihlar, A. Surca Vuk, B. Orel and G.Drazic, Solid State Ionics, 165 (2003) 191-200.

[9] B. Sasi and K. G. Gopalchandran, Nanotechnology, 18 (2007) 115613.

[10] H. Kamel, E. K. Elmaghraby, S. A. Ali, K. Abdel- Hady, Thin Solid Films, 483(2005) 330-339.

[11] P. Puspharajah, S. Radhakrshna, A. K. Arof, J. Mater. Sci., 32 (1997) 3001-3006.

[12] L.D. Kadam, P.S. Patil, Solar Energy Materials and Solar Cells, 69 (2001) 361–369.

[13] A. Agrawal, H. R. Habibi, R. K. Agrawal, J. P. Cronin, D. M. Roberts, C. P. R'Sue, C. M. Lampert, Thin Solid Films, 221 (1992) 239-253.

[14] M. Tanaka, M. Mukai, Y. Fujimori, M. Kondoh, Y. Tasaka, H. Baba, S. Usami, Thin Solid Films, 281-282 (1996) 453-456.

[15] M.A. Vidales-Hurtado and A. Mendoza- Galv´an, Materials Chemistry and Physics, 107 (2008) 33.

[16] E.Ozkan, I. Turhan, F.Z. Tepehan, N. Ozer, Solar Energy Materials and Solar Cells, 92 (2008) 164-196.

[17] Eiji Fujii, Atsushi Tomozawa, Hideo Torii, Ryoichi Takayama, Jpn. J. Appl. Phys, 35 (1996) 328- 330.

[18] Hao-Long Chen, Yang-Ming Lu, Weng-Sing Hwang, Surface and Coatings Technology,198(2005) 138.

[19] S. C. Chen, T. Y. Kuo, Y. C. Lin, C. L. Chang, Adv. Mater. Res. 123-125 (2010) 181-184.

[20] J. Park, K. Ahn, Y. Nah, H. Shim Y. Sung, J. Sol-Gel Sci. and Tech., 31 (2004) 323-328.

[21] Seok-Soon Kim, Kyung-Won Park, Jun-Ho Yum, Yung-Eun Sung, Solar Energy Materials and Solar Cells, 90 (2006) 283–290.

[22] F. Atay, S. Kose, V. Bilgin, I. Akyuz, Turk. J. Phys., 27 (2003) 285-291.

[23] X. Liu, G. Qiu, Z.Wang, X. Li, Nanotechnology, 16 (2005) 1400.
[24] F. I. Ezema, A.B.Ekwealor, R.U. Osuji, Turk. J. Phys. 30 (2006)157.
[25] Han, X., Liu, R., Chen, W., Xu, Z, Thin Solid Films, 516 (2008) 4025-4029.
[26] N.A. Subrahamanyam, "A textbook of Optics", Brj Laboratory, Delhi, 1977.
[27] T.S. Moss, G.J. Burrell, B. Ellis, "Semiconductor Opto-Electronics, Wiley, New York, 1973.