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Spray pyrolysis deposition and effect of annealing temperature on urbach energy and dispersion parameters 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 absorbance of prepared thin films determined by UV-Visible spectrophotometer in the range of 380-900 nm. The absorbance increased with increasing annealing temperature until 550 nm, and then don't change at the wavelength greater than 550 nm. While the reflectance, real and imaginary dielectric constant, and optical conductivity decreased with increasing annealing temperature until 550 nm. Dispersion parameters that studied decreases with increasing annealing temperature, while the Urbach energy increased with increasing annealing temperature. © 2015 Trade Science Inc. - INDIA

KEYWORDS

NiO thin films;
Annealing;
Eurbach energy;
Dispersion parameters.

INTRODUCTION

Transparent conducting oxides (TCO) are well known and have been widely used in optoelectronics and transparent electronics as well as in different research fields. Most of the existing TCOs are n-type, whereas it is very difficult to prepare binary metal oxides with p-type conductivity[1]. Nickel oxide (NiO) is a promising p-types semiconducting oxide material[2-3] having a wide band gap of 3.6 eV to 4eV[4]. Nickel oxide is one of the most popular electro chromic materials after tungsten oxide. As an electro chromic material, NiO has particular advantages owing to its high electro chromic efficiency, cyclic reversibility, durability and grey coloration, which are useful for smart windows technology[5-7]. Thin films are prepared by various methods, such as; sputtering, pulsed laser deposition[8], electron-beam evaporation, and chemical methods[9], atomic layer epitaxy, sol gel, spray pyrolysis[10], spin coating[11]. Among various methods, spray pyrolysis is one through which the films can be coated for large area.

In the present work, the effect of annealing temperature on the Urbach energy and dispersion parameters of Cu-doped NiO films deposited by chemical spray pyrolysis is considered.

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 ($NiCl_2.6H_2O$) (from sigma-Aldrich company), into 100 ml of redistilled water to make 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 rate0.2 ml /spray, substrate to nozzle30 cm, spraying time during each cycle 7 sec, time interval between successive sprays1.5 min, and the carrier gas (filtered compressed air) was 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, then optical transmittance and absorbance were recorded in the wavelength range (380-900nm) using UV-Visible spectrophotometer (Shimadzu Company Japan) double beam spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the absorbance spectra in the range of 300-900 nm recorded by UV-Visible spectrophotometer (Shimadzu Company Japan) double beam spectrophotometer, for Cu-doped NiO thin films. From this figure, it can notice that the absorbance increases with increasing annealing temperature until 600 nm and then do not change at the wavelength greater than 550 nm.

The reflectance spectra are shown in Figure 2 of Cu-doped NiO thin film for various annealing temperature. This figure shows the decreases of reflectance with increasing annealing temperature until 550 nm and increases with wavelength, and then the reflectance increases slightly at the wavelength greater than 550 nm and decreases with wavelength.

Figure 3 and Figure 4 are representing the relationship between real and imaginary dielectric constants with wavelength for Cu-doped NiO thin film for various annealing temperature that calculated from the following formulas[12]:

$$\varepsilon_1 = n^2 - k^2 \quad (1)$$

$$\varepsilon_2 = 2nk\ 2 \quad (2)$$

From these figures it can show the real and imaginary dielectric constants are decreased with increasing annealing temperature and increases with increasing wavelength until 550 nm, and at wavelength greater than 550 nm, the real and imaginary dielectric constants are increased with increasing annealing temperature and decreases with increasing wavelength.

Figure 5 represents the relationship between optical conductivity ($\sigma_{optical}$) and wavelength for Cu-doped NiO thin film that calculated from the following relation[13]:

$$\sigma_{optical} = \frac{\alpha nc}{4\pi} \quad (3)$$

Where α is the absorption coefficient, n is the refractive index, and c is the velocity of light. From Figure 5 it can notice the optical conductivity decreases with increasing annealing temperature until 550 nm, and then at the wavelength greater than 550 nm, the optical conductivity increased with increasing annealing temperature.

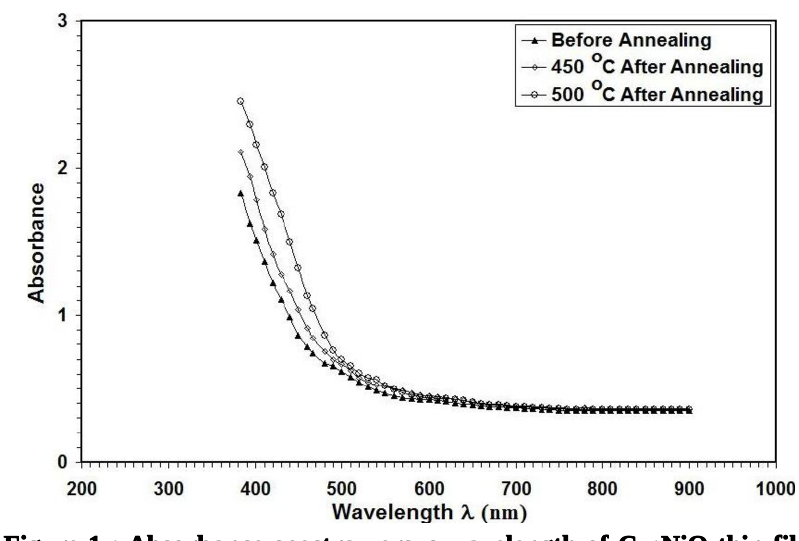

Figure 1 : Absorbance spectra versus wavelength of Cu:NiO thin film

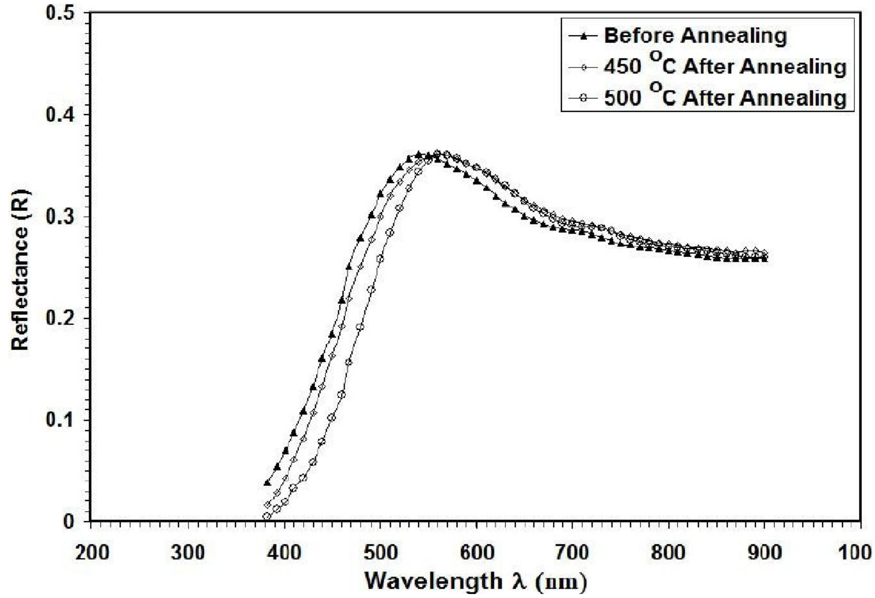

Figure 2 : Reflectance versus wavelength of Cu:NiO thin film

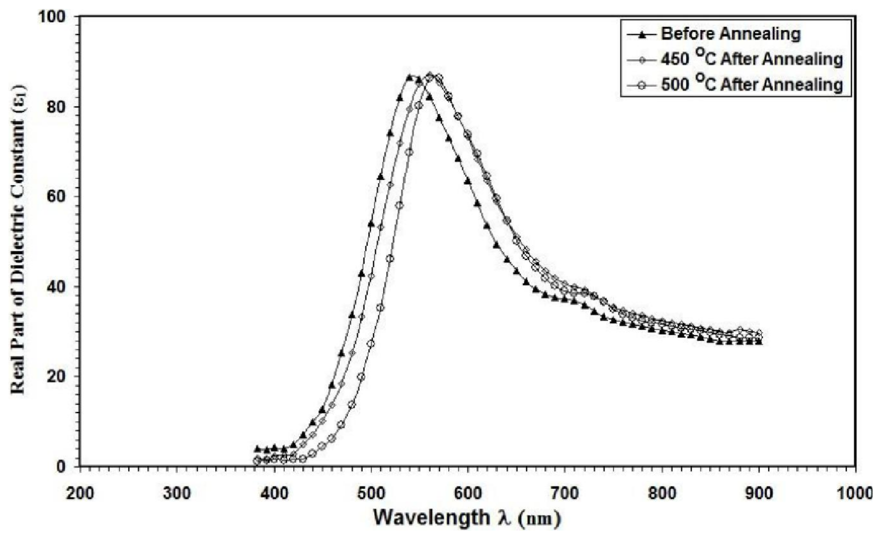

Figure 3 : Real part of dielectric constant versus wavelength of Cu:NiO thin film

It is known that the absorption coefficient near the band edge shows an exponential dependence on photon energy[14]:

$$\alpha(\lambda) = \alpha_o \exp\left(\frac{h\upsilon}{E_U}\right) \quad (4)$$

Where E_U is the Urbach energy that corresponds to the width of the band tail and can be evaluated as the width of the localized states, α_o is a constant, and hυ is the photon energy. Thus, a plot of In [α(λ)] versus photon energy should be linear and Urbach energy can be obtained from the slope.

In order to analyze the refractive index dispersion of the Cu-doped NiO thin films, it used the single-oscillator model, developed by DiDomenico and Wemple[15]. The single-oscillator model for the refractive index dispersion is expressed as follows[15]:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\upsilon)^2} \quad (5)$$

Where n is the refractive index, E_o is the single-oscillator energy for electronic transitions and E_d is the dispersion energy which is a measure of the strength of inter band optical transitions. The oscillator energy E_o is an average of the optical band gap (E_g), can be obtained from the Wemple–DiDomenico model[16].

Experimental verification of Eq.4 can be obtained by plotting $(n^2-1)^{-1}$ vs. $(h\upsilon)^2$ as illustrated in

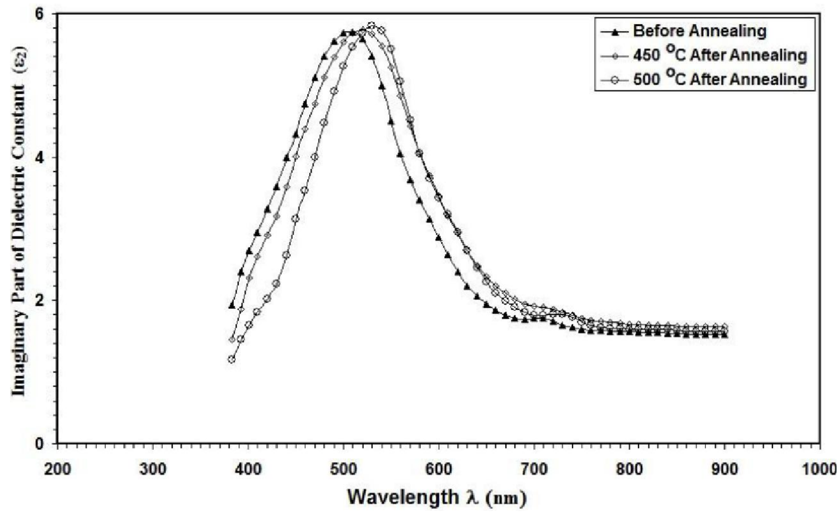

Figure 4 : Imaginary part of dielectric constant versus wavelength of Cu:NiO thin film

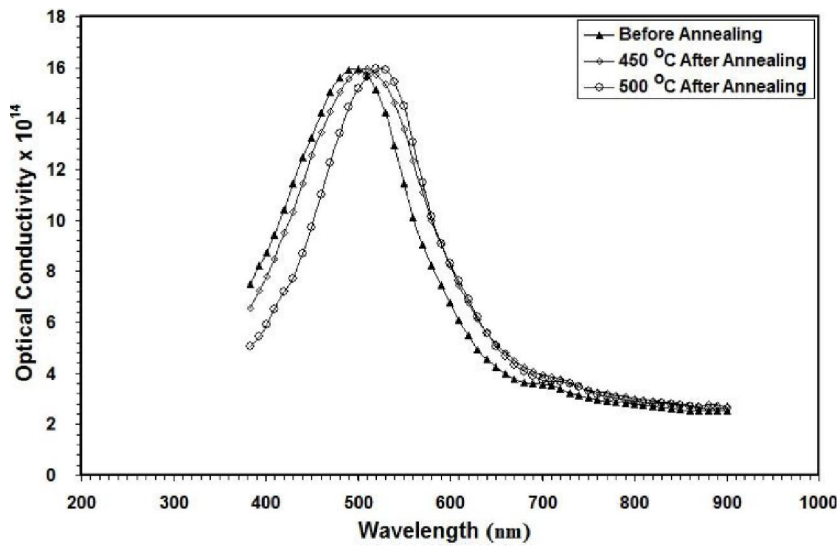

Figure 5 : Optical conductivity versus wavelength of Cu:NiO thin film

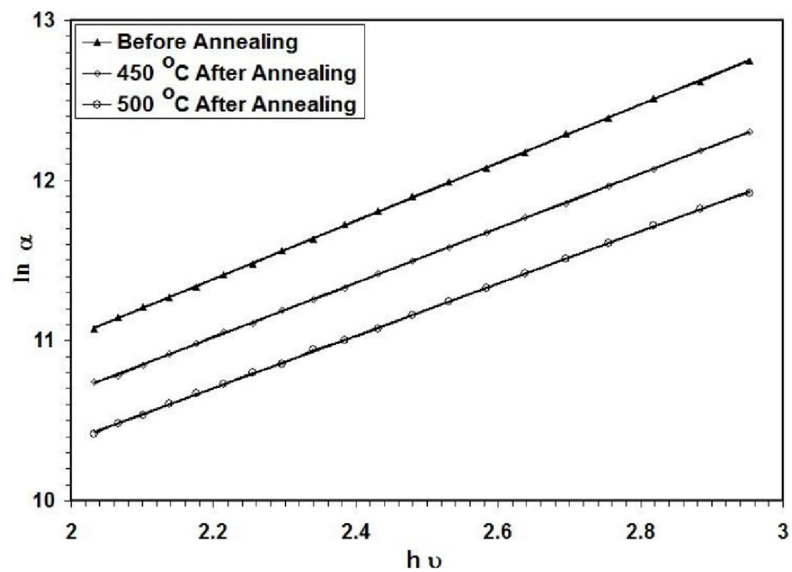

Figure 6 : Plot of lnα versus hυ of Cu:NiO thin film

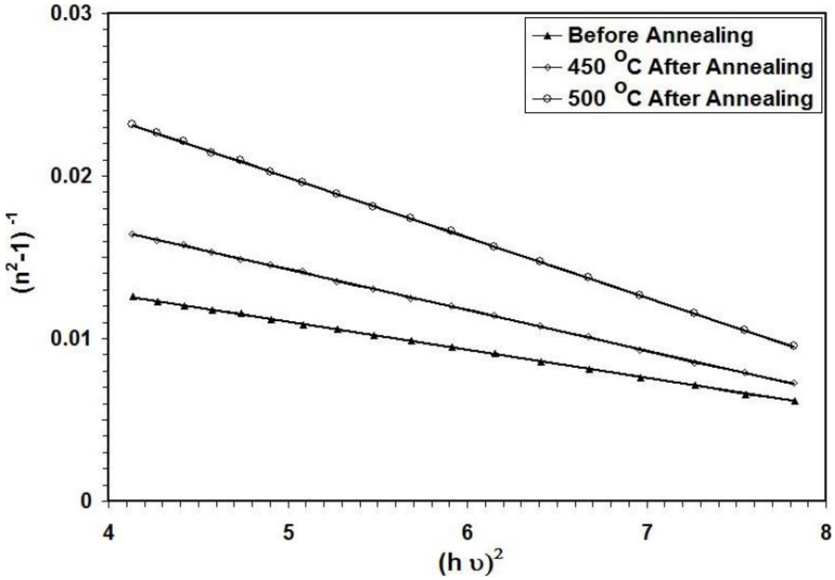

Figure 7 : Plot of $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ of Cu:NiO thin film

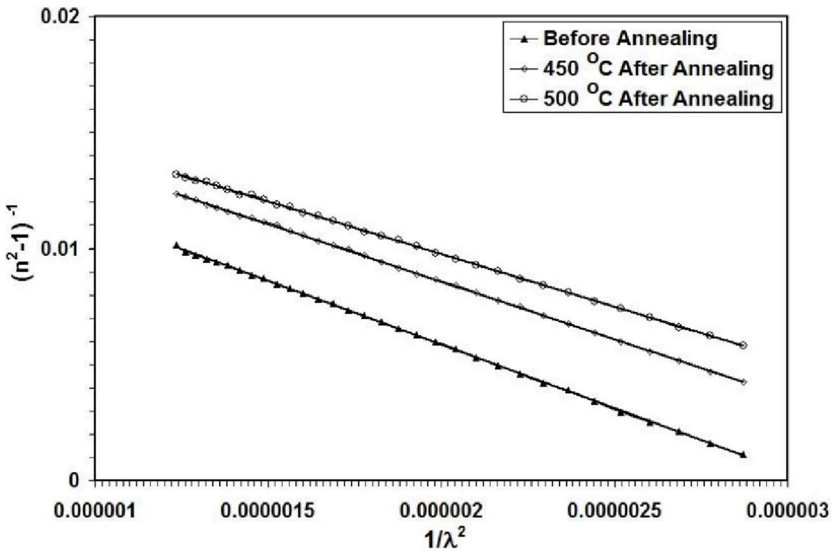

Figure 8 : Plot of $(n^2-1)^{-1}$ versus $(h\upsilon)^2$ of Cu:NiO thin film

TABLE 1 : The optical parameters of Cu-doped NiO thin film for various annealing temperature

Sample	E_d (eV)	E_o (eV)	E_g (eV)	ε_∞	n(o)	M_{-1}	M_{-3} eV^{-2}	S_o x10^{13} m^{-2}	?$_o$ nm?	U_E meV
Before Annealing	48.31	5.80	2.90	9.33	3.05	8.33	0.247	6.10	404	555
450 °C After Annealing	33.31	5.66	2.83	6.88	2.62	5.88	0.183	6.71	367	588
500 °C After Annealing	24.23	5.58	2.78	5.34	2.31	4.34	0.139	7.39	322	625

Figure 7.

The refractive index has been analyzed to yield the high frequency dielectric constant ($\varepsilon_\infty = n_\infty^2$)[17-18]. Assuming the high-frequency properties could be treated as a single oscillator at wavelength (λ_o) at high frequency. The high-frequency dielectric constant can be calculated by applying the following simple classical dispersion relation[18]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \quad (6)$$

The S_o and λ_o values were obtained from the slope of $1/S_o$ and intercept of $(S_o\lambda_o^2)^{-1}$ of the curves plotted.

The imaginary complex dielectric constant (ε_i)

parameter includes the desired response information about electronic and optical properties of the optical material.

The M_{-1} and M_{-3} moments of the optical spectrum can be obtained from the following relations[19]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (7)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (8)$$

CONCLUSIONS

Cu:NiO thin films onto glass substrate prepared by spray pyrolysis method. The reflectance, real and imaginary dielectric constant, and optical conductivity decreased with increasing annealing temperature until 550 nm. Dispersion parameters such as E_d, E_o, E_∞, n (0), M_{-1}, M_{-3}, and λ_o decrease with increasing annealing temperature, while the Urbach energy increased with increasing annealing temperature that inversely proportion with energy gap.

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