

Effect of Cu-doping on Urbach Energy and Dispersion Parameters of Cu:NiO Film deposited by CSP

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ABSTRACT

This work presents the effect of Cu-doping on Urbach energy and dispersion parameters 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 absorbance and optical conductivity increased with increasing Cu-doping in the prepared films. Dispersion parameters that studied are decreased with increasing Cu-doping while Urbach energy increased.

Keywords: Dispersion Relation; NiO Thin Films; Urbach Energy

1. INTRODUCTION

The traditional TCO thin films such as Sn-doped In_2O_3 , Al-doped ZnO, and Sb-doped SnO_2 have been widely studied. However, these traditional TCO often shows n-type conductivity and there is lack of p-type TCO thin film. NiO is a p-type TCO with an energy gap of 3.15 to 4.0eV[1]. The optical constants (refractive index n and extinction coefficient k) and the film thickness are important parameters that affect the performance of an optical film in an optical system[2] and the optical simulation results are strongly dependent on the optical constants of the films [3]. NiO films are suitable for magnetoresistance sensors, chemical sensors [4-5], electrochromic devices [6] and transparent p-type semi conducting layer, smart windows [7] and dye-sensitized photo cathodes [8-10].

Thin film of nickel oxide can be produced by different methods such as evaporation, sputter deposition, sol gel, electrochemical and chemical techniques [11-17]. 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 [18].

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

2. EXPERIMENTAL DETAILS

Nickel nitrite $\text{Ni}(\text{NO}_2)_2$ was used as a source of NiO, for the doping agent $\text{Cu}(\text{CH}_3\text{COO})_4$ was adopted to prepare CuO in the percentage of 2% and 4%. These chemicals dissolved in 100 ml of re-distilled water to form an aqueous solution which was used to maintain the desired films on a microscopic glass slides the optimum parameters of the preparation conditions were arrived at the following: substrate temperature 400°C , spraying rate 4ml/min, substrate to nozzle was 30 ± 1 cm, time period for spraying was 8 s, time interval waiting was 2min between, and filtered air as carrier gas was maintained at a pressure of 10^5 Pascal.

Film thickness was measured by gravimetric and was found to be 350 ± 20 nm. The Films were annealed at ($450, 500$) $^\circ\text{C}$ respectively. then optical transmittance was recorded in the wavelength range (380-900)nm by a Double beam UV-Visible spectrophotometer (Shimadzu Company Japan).

3. RESULTS AND DISCUSSION

Absorbance spectra that recorded by using UV-Visible spectrophotometer in the range 380-900 nm are determined in Fig.1 of Cu:NiO thin film. From this figure, it can notice the increases of absorbance with increasing Cu additive in the Cu:NiO thin films. This behavior can be attributed to the formation of secondary levels in the band structure. While the reflectance that shown in Fig. 2 take other behavior depend on wavelength.

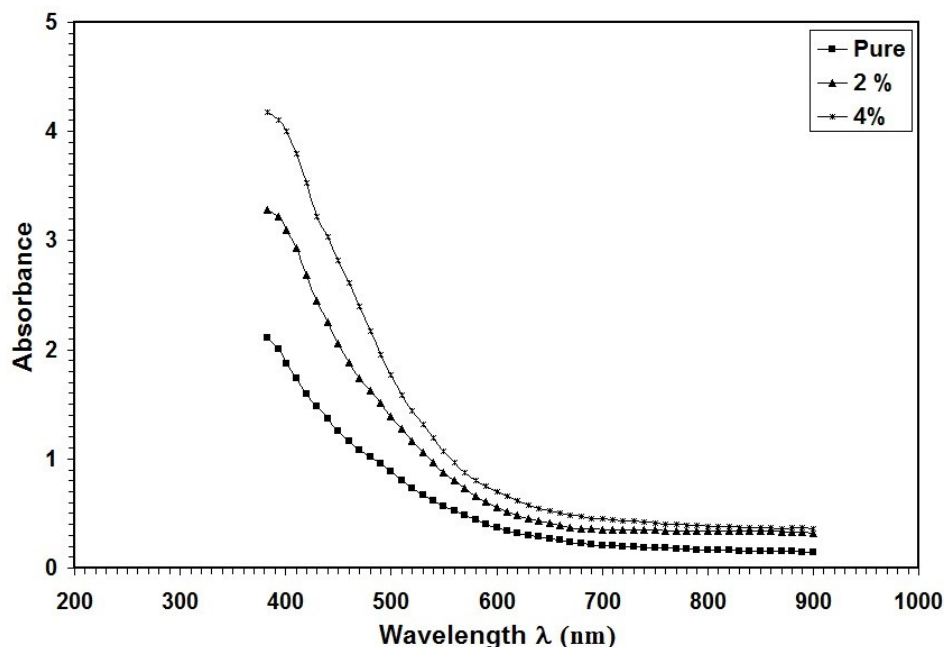


Fig. 1. Plot of absorbance spectra vs wavelength of Cu:NiO thin film.

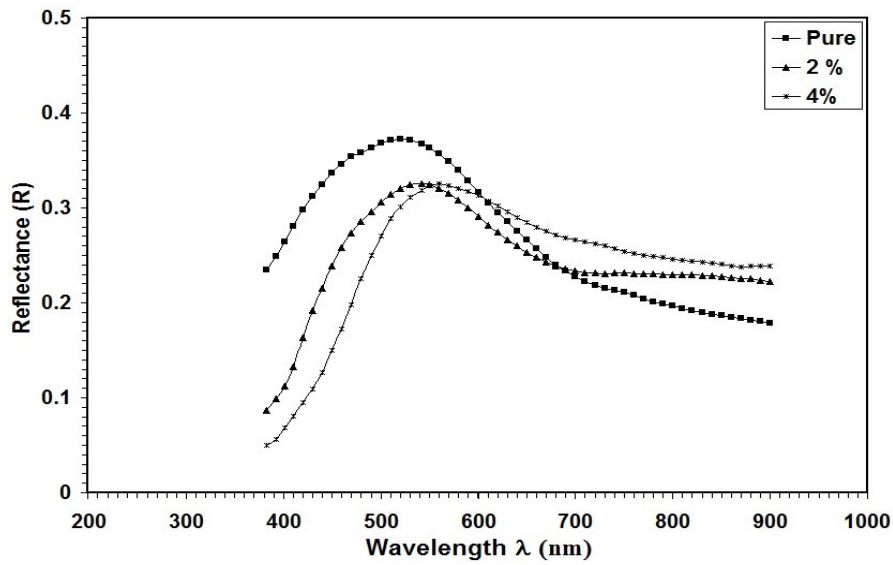


Fig. 2. Plot of reflectance spectra vs wavelength of Cu:NiO thin film.

Real (ϵ_1) and imaginary (ϵ_2) dielectric constants are determined from the following relations [19]:

$$\epsilon_1 = n^2 - k^2 \quad (1)$$

$$\epsilon_2 = 2nk \quad (2)$$

Where n is the refractive index and k is the extinction coefficient. Figs.3-4 shows the behavior of real and imaginary dielectric constant with wavelength. From these figures it can notice that the dielectric constant increases with increasing Cu additive in Cu:NiO thin films at wavelength greater than 500 nm.

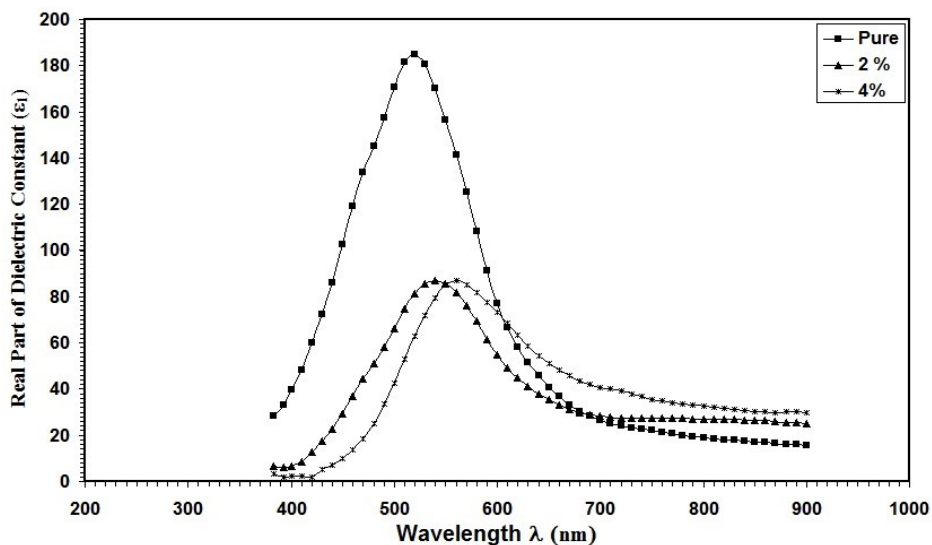


Fig. 3. Plot of real part of dielectric constant vs wavelength of Cu:NiO thin film.

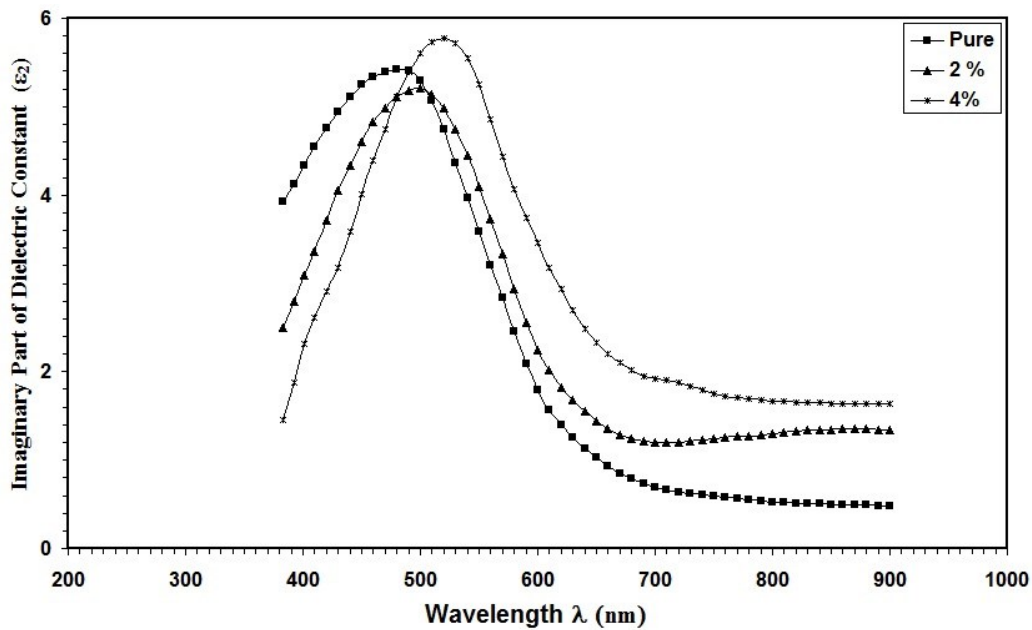


Fig. 4. Plot of imaginary part of dielectric constant vs wavelength of Cu:NiO thin film.

Optical conductivity behavior is represented in Fig.5. From this figure, it can notice that the optical conductivity increases with increasing Cu additive in Cu:NiO thin films at wavelength greater than 500 nm.

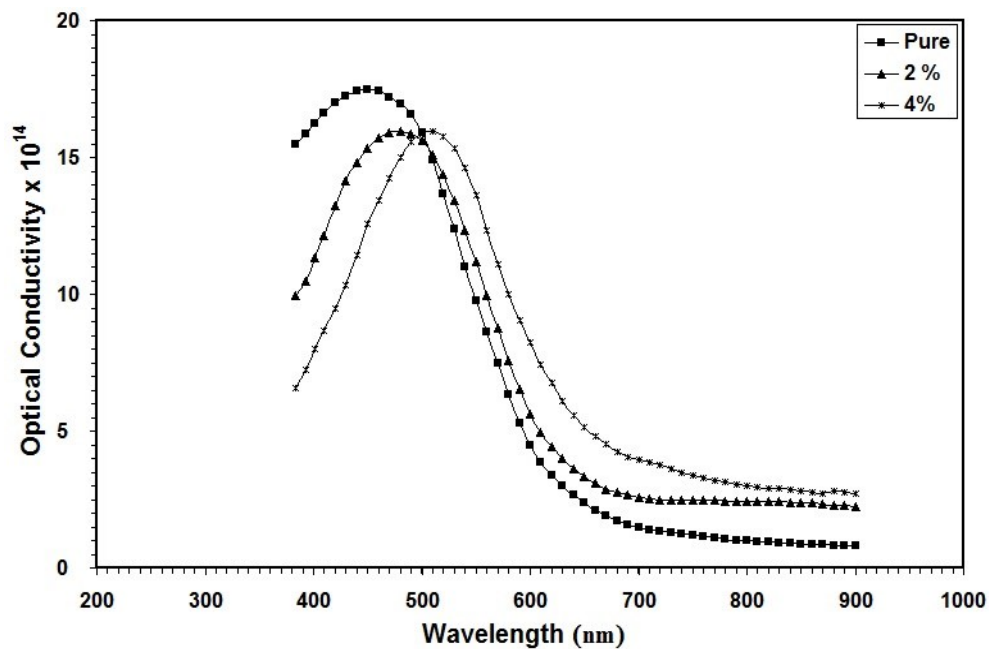


Fig. 5. Plot of optical conductivity vs wavelength of Cu:NiO thin film.

The observed exponential sub-band gap absorption tails in experimentally measured optical spectra were explained using the Urbach–Martienssen rule[20-21]with the following mathematical formulation:

$$\alpha = \alpha_o \left(\frac{E_o}{E_U} \right) \quad (3)$$

The parameter E_o corresponds to the energy of the lowest free excited state at zero lattice temperature, while E_u is the Urbach energy. This parameter determines the steepness of the Urbach tail.

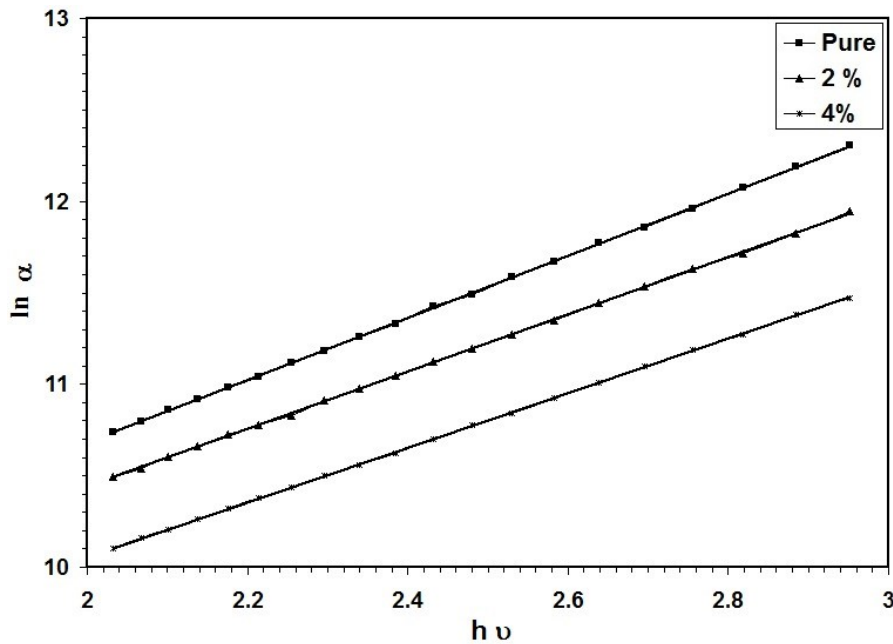


Fig. 6. Plot of $\ln \alpha$ vs $h\nu$ of Cu:NiO thin film.

Plotting $(n^2-1)^{-1}$ vs. $(h\nu)^2$ allows us to determine the oscillator parameters. E_o and E_d values were calculated from the slope and intercept on the vertical axis of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ plot, as shown in Fig.

The refractive index n_∞ at infinite wavelength can be determined by the following relation [22]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda} \right)^2 \quad (4)$$

The plot of $(n^2-1)^{-1}$ vs. λ^{-2} was plotted to obtain n_∞ value of Cu-doped NiO thin films. The intersection with $(n^2-1)^{-1}$ axis is $(n_\infty^2-1)^{-1}$ and hence, n_∞^2 at λ_o equal to ϵ_∞ (high-frequency dielectric constant).

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 M_{-1} and M_{-3} moments of the optical spectra can be obtained from the following relations [23]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (5)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \quad (6)$$

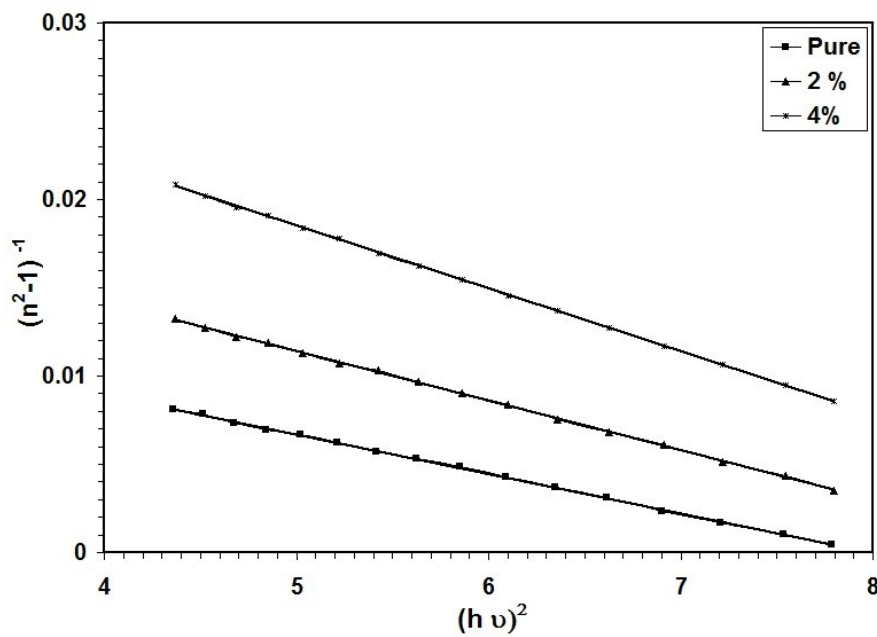


Fig. 7. Plot of $(n^2-1)^{-1}$ vs $(h\nu)^2$ of Cu:NiO thin film.

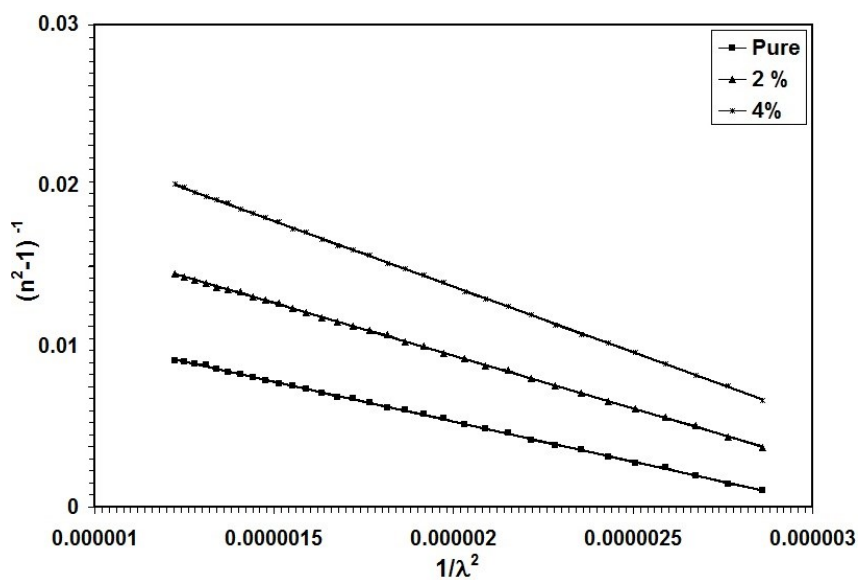


Fig. 8. Plot of $(n^2-1)^{-1}$ vs $1/\lambda^2$ of Cu:NiO thin film.

Table 1. The optical parameters of Cu:NiO thin films.

Sample	E_d (eV)	E_o (eV)	E_g (eV)	ϵ_∞	$n(0)$	M_{-1}	M_{-3} eV^{-2}	S_o $\times 10^{13}$ m^{-2}	λ_o $\nu\mu$	U_E meV
Pure	51.8	6.20	3.100	9.30	3.05	8.30	0.215	7.64	361	584
2%	34.0	6.12	3.060	6.55	2.56	5.55	0.148	5.53	347	641
4%	26.4	5.81	2.905	5.54	2.35	4.54	0.134	4.69	326	671

4. CONCLUSION

The effect of Cu-doping on Urbach energy and dispersion parameters of Cu:NiO thin film is studied. The absorbance and optical conductivity increased with increasing Cu-doping in the prepared films. Dispersion parameters such as E_d , E_o , E_∞ , $n(0)$, M_{-1} , M_{-3} , S_o , and λ_o are decreased with increasing Cu-doping while Urbach energy increased.

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