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$_2$O$_3$, 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 \( \text{Ni(NO}_2\text{)}_2 \) was used as a source of NiO, for the doping agent \( \text{Cu(CH}_3\text{COO)}_4 \) 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 \(^\circ\text{C}\), 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.
Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constants are determined from the following relations [19]:

$$\varepsilon_1 = n^2 - k^2$$  \hspace{1cm} (1)

$$\varepsilon_2 = 2nk$$  \hspace{1cm} (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.
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.
The observed exponential sub-band gap absorption tails in experimentally measured optical spectra were explained using the Urbach–Martenssen rule[20-21] with the following mathematical formulation:

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

(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.](image)

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 $n_\infty$ at infinite wavelength can be determined by the following relation [22]:

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

(4)

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

The $S_o$ and $\lambda_o$ 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]:

\[
E_o^2 = \frac{M_{-1}}{M_{-3}} \tag{5}
\]

\[
E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{6}
\]

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 | Ed (eV) | Eo (eV) | Eg (eV) | E∞ | n(0) | M-1 | M-3 eV^-2 | S0 x10^13 m^-2 | λo | 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 Ed, Eo, E∞, n(0), M-1, M-3, S0, and λo are decreased with increasing Cu-doping while Urbach energy increased.

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