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 magnetores istance 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 Ni(NO$_2$)$_2$ was used as a source of NiO, for the doping agent Cu(CH$_3$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 4 ml/min, substrate to nozzle was 30±1 cm, time period for spraying was 8 s, time interval waiting was 2 min 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) °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.

![Absorbance Spectra](./fig1.jpg)

**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 ($\varepsilon_1$) and imaginary ($\varepsilon_2$) dielectric constants are determined from the following relations [19]:

$$\varepsilon_1 = n^2 - k^2$$  \hspace{0.5cm} (1)

$$\varepsilon_2 = 2nk$$  \hspace{0.5cm} (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.
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:

\[ \alpha = \alpha_0 \left( \frac{E_o}{E_u} \right) \]  

(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 \((n^2-1)^{-1}\) and hence, \( n_\infty^2 \) at \( \lambda_o \) equal to \( \varepsilon_\infty \) (high-frequency dielectric constant).

The \( S_0 \) and \( \lambda_o \) values were obtained from the slope of \( 1/S_0 \) and intercept of \((S_0 \lambda_o^2)^{-1}\) 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 $(\hbar \nu)^2$ 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_d$ (eV)</th>
<th>$E_o$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$E_\infty$</th>
<th>$n(0)$</th>
<th>$M_1$</th>
<th>$M_3$ eV$^{-2}$</th>
<th>$S_0 \times 10^{13}$ m$^{-2}$</th>
<th>$\lambda_\infty$ meV</th>
<th>$U_E$ meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>51.8</td>
<td>6.20</td>
<td>3.100</td>
<td>9.30</td>
<td>3.05</td>
<td>8.30</td>
<td>0.215</td>
<td>7.64</td>
<td>361</td>
<td>584</td>
</tr>
<tr>
<td>2%</td>
<td>34.0</td>
<td>6.12</td>
<td>3.060</td>
<td>6.55</td>
<td>2.56</td>
<td>5.55</td>
<td>0.148</td>
<td>5.53</td>
<td>347</td>
<td>641</td>
</tr>
<tr>
<td>4%</td>
<td>26.4</td>
<td>5.81</td>
<td>2.905</td>
<td>5.54</td>
<td>2.35</td>
<td>4.54</td>
<td>0.134</td>
<td>4.69</td>
<td>326</td>
<td>671</td>
</tr>
</tbody>
</table>

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 $E_d$, $E_o$, $E_\infty$, $n(0)$, $M_1$, $M_3$, $S_0$, and $\lambda_\infty$ are decreased with increasing Cu-doping while Urbach energy increased.

References


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