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Engineering the properties of NiO thin films by copper incorporation for optoelectronic applications

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In the present work, nickel oxide (NiO) thin films were successfully deposited on glass substrates using the spray pyrolysis technique. The effect of copper (Cu) doping on the structural, optical, and electrical properties of the films was systematically investigated. All Cu doped NiO thin films exhibited a cubic crystal structure with a preferred orientation along the (111) plane. The minimum crystallite size of 22.45 nm was obtained at a Cu concentration of 6 at.%. This indicates improved crystallinity and enhanced structural ordering compared with the other films. The average optical transmittance varied between 67% and 87% in the visible region. The band gap energy decreased from 3.43 to 3.60 eV and the Urbach energy increased from 0.523 to 0.935 eV, as the Cu doping increased from 0 to 12 at.%. This indicates that the observed behavior can be attributed to the formation of impurity levels and defect states within the band gap, which facilitate optical transitions at lower energies. Electrical measurements showed a maximum conductivity of 2.916 $(\Omega.cm)^{-1}$ at 12 at.% Cu, indicating improved charge carrier transport. However, the enhancement in structural, optical, and electrical properties suggests that Cu doped NiO thin films are promising candidates for optoelectronic applications, particularly as window layers in solar cells.

Keywords: Nickel oxide; XRD patterns; Thin films; optical properties; electrical conductivity.

Модифікація властивостей тонких плівок NiO шляхом легування міддю для оптоелектронних застосувань. *Saliha Bouaicha, Okba Belahssen, Mebrouk Ghougali, Said Benramache, Abdelghani Lakel*

У цій роботі методом розпилювального піролізу на скляні підкладки було успішно нанесено тонкі плівки оксиду нікелю (NiO). Було проведено систематичне дослідження впливу легування міддю (Cu) на структурні, оптичні та електричні властивості цих плівок. Усі леговані міддю плівки NiO мали кубічну кристалічну структуру з переважною орієнтацією вздовж площини (111). Мінімальний розмір кристалітів (22,45 нм) було отримано при концентрації Cu 6 ат.%, що свідчить про покращену кристалічність і вищий ступінь структурного впорядкування порівняно з іншими зразками. Середнє оптичне пропускання у видимій області спектра варіювалося в межах 67–87%. При збільшенні вмісту Cu від 0 до 12 ат.% ширина забороненої зони зменшувалася від 3,60 до 3,43 еВ, а енергія Урбаха зростала від 0,523 до 0,935 еВ. Це вказує на те, що спостережувані зміни зумовлені утворенням домішкових

рівнів і дефектних станів у межах забороненої зони, які полегшують оптичні переходи при менших енергіях. Результати електричних вимірювань показали, що максимальна провідність (2,916 (Ом·см)$^{-1}$) досягається при вмісті Cu 12 ат.%, що свідчить про покращення транспорту носіїв заряду. Таким чином, покращення структурних, оптичних та електричних характеристик дозволяє розглядати леговані міддю плівки NiO як перспективні матеріали для оптоелектронних застосувань, зокрема як віконні шари в сонячних елементах.

1. Introduction

Nickel oxide (NiO) is one of the most extensively studied metal oxides owing to its low cost, excellent chemical stability, and wide range of applications in catalysis, transparent conducting oxides, electrochromic devices, photodetectors, gas sensors, photovoltaic devices, supercapacitors, heat reflectors, photoelectrochemical cells, solar cells, and other optoelectronic systems [1–5]. NiO is a wide band gap oxide that can function as a transparent *p*-type semiconductor, with a band gap energy typically ranging from 3.45 to 3.85 eV [6, 7]. Its tunable structural, optical, and electrical properties further enhance its potential, making it a promising material for advanced electronic and photovoltaic applications.

A variety of techniques have been employed for the synthesis and fabrication of copper-doped nickel oxide (NiO:Cu) nanostructures, aiming to optimize its structural, optical, and electrical characteristics for advanced applications, including thermal evaporation, sputtering, pulsed laser ablation, thermal decomposition, electrochemical deposition, and sol–gel methods [8–12]. In recent years, spray-based techniques have attracted considerable attention due to their simplicity, low cost, and suitability for large-area deposition.

Doping NiO with transition metals, such as copper, is an effective strategy to improve its crystallinity, optical transparency, and electrical conductivity. Copper incorporation can modify the carrier concentration, lattice structure, and band gap energy, enhancing the overall performance of the films. The aim of this work is to obtain the Cu doped NiO thin films on glass substrates by spray pyrolysis, and to study the effect of varying copper concentrations on their structural, optical, and electrical properties. By examining factors such as crystallinity, optical transmittance, optical band gap, Urbach energy and electrical conductivity, this study provides valuable insights and a novel perspective, making it easier for readers from different countries to enhance their intellectual and scientific skills.

In this work, a low-cost spray pyrolysis technique was employed to prepare NiO:Cu thin films with copper concentrations of 0, 3, 6, 9, and 12 at.%. The Cu-doped NiO solution was prepared by dissolving nickel nitrate and copper nitrate in double-distilled water as the solvent. Subsequently, the Cu-doped NiO films were then deposited at 480 °C for two minutes.

2. Experimental details

Cu doped NiO thin films were prepared onto thoroughly cleaned glass substrates using pneumatic spraying technique. Nickel nitrate hexahydrate, 99.999% ($Ni(NO_3)_2$, $6H_2O$) and copper nitrate trihydrate ($Cu(NO_3)_2$, $3H_2O$) were dissolved in double-distilled water as a solvent, while two drops of HCl were added as a stabilizing agent for all samples prepared in this work. The molar concentrations of the nickel nitrate and copper nitrate precursor solutions were both 0.20 mol L^{-1}. The two solutions were mixed in appropriate volume ratios to obtain Cu/(Ni +Cu) atomic ratios of 0, 3, 6, 9 and 12 at.%. The resulting mixture was stirred at 60 °C for 30 min to obtain a clear and homogenous solution and was subsequently cooled to room temperature. Prior to deposition, the glass substrates were cleaned sequentially with acetone, alcohol, and deionized water, and then dried using a hot-air dryer.

The precursor solution was sprayed onto ordinary glass substrates maintained at 480 °C for 2 minutes using an intermittent mode, which allowed the substrate temperature to remain stable throughout the deposition process. The spraying was carried out using an air-assisted nebulizer system, in which the solution was atomized into a fine and uniform droplet stream. Upon reaching the heated substrate surface, the droplets underwent thermal decomposition, resulting in the gradual formation of a thin film.

X-ray diffraction (XRD) analysis was performed to examine the structural properties of the Cu doped NiO thin films. The measurements were carried out using a BRUKER AXS-8D diffractometer equipped with CuKα radiation (λ = 0.15406 nm), operating at an acceler-

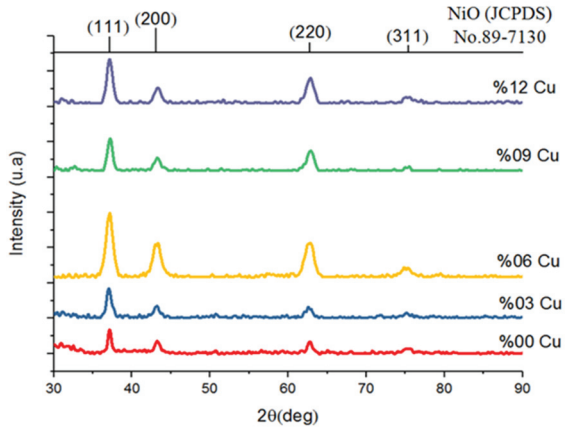

Figure 1. XRD patterns of deposited Cu doped NiO thin films on a glass substrate at different copper concentrations.

ating voltage of 40 kV and a current of 40 mA. The diffraction patterns were recorded over a 2θ range from 30 degrees to 90 degrees. The optical transmittance of the Cu doped NiO films was measured in the wavelength range of 300–900 nm using a UV–visible spectrophotometer (PerkinElmer Lambda 25).

3. Results and discussion

3.1. Structural properties

X-ray diffraction (XRD) analysis was used to study the structural properties of Cu doped NiO thin films deposited with varying copper concentrations. The XRD patterns of all samples are presented in Figure 1. As shown, all films exhibit a prominent diffraction peak near 2θ ≈ 37 deg, corresponding to the (111) preferred orientation, along with additional peaks indexed to the (200), (220), and (311) planes. These results are consistent with the standard data reported in the Joint Committee of Powder Diffraction Standards (JCPDS) card No. 89-7130. The observed peak positions confirm that the films possess a cubic crystalline structure, in agreement with previously reported studies [13,14]. No additional peaks related to copper or secondary phases were detected in the diffraction patterns. This can be attributed to the low doping concentrations, which typically do not generate new diffraction peaks but instead induce slight variations in the lattice parameters of the host material. Such variations are often associated with lattice strain resulting from the incorporation of dopant ions into the crystal structure [15]. According to the Williamson–Hall (W–H) method, the broadening of diffraction peaks is considered to arise from both crystallite size and lattice strain contributions, assuming a Lorentzian peak profile.

Based on this assumption, a mathematical relationship is established between the full width at half maximum intensity β, average crystallite size D and the microstrain ε according to the following formula [16]:

$$\beta\cos\theta = \frac{0.9\lambda}{D} + 4\varepsilon\sin\theta \qquad (1)$$

where λ is the X-ray wavelength (λ=0.154060 nm for CuKα radiation), β is the full-width at half-maximum (FWHM) in radians, and θ is the diffraction peak angle.

Figure 2 presents the Williamson–Hall (W–H) plot of βcosθ versus 4sinθ, from which the microstrain (ε) can be determined from the slope; while the crystallite size (D) is obtained from the y-intercept. If the data points in the W–H plot are scattered, meaning that βcosθ does not vary linearly with 4sinθ, then the peak broadening is considered anisotropic [16]. The calculated values of the average crystallite size and microstrain for all Cu doped NiO thin films are summarized in Table 1. The crystallite sizes were found to vary from 22.45 to 39.08 nm, reflecting variations due to copper doping.

Figure 3 illustrates the variation of crystallite size (D) and microstrain (ε) of Cu doped NiO thin films as a function of copper concentration. It is observed that the crystallite size initially decreases from about 39 nm at 0 at.% Cu to a minimum value of about 22–23 nm at 6 at.%, then slightly increases at higher doping levels before decreasing again at 12 at.%. In contrast, the microstrain shows an opposite trend, increasing from approximately 0.11% to a maximum of about 0.32% at 6 at.%, followed by a gradual decrease. This inverse relationship between D and ε is consistent with the Williamson–Hall method, indicating that the incorporation of Cu ions into the NiO lattice induces

Table 1. Structural parameters of Cu doped NiO thin films at different Cu concentrations.

Cu concentrations (at.%)	0	3	6	9	12
Crystallite size D (nm)	39.08	28.68	22.45	27.22	24.46
Microstrain ε (%)	0.112	0.194	0.316	0.240	0.215

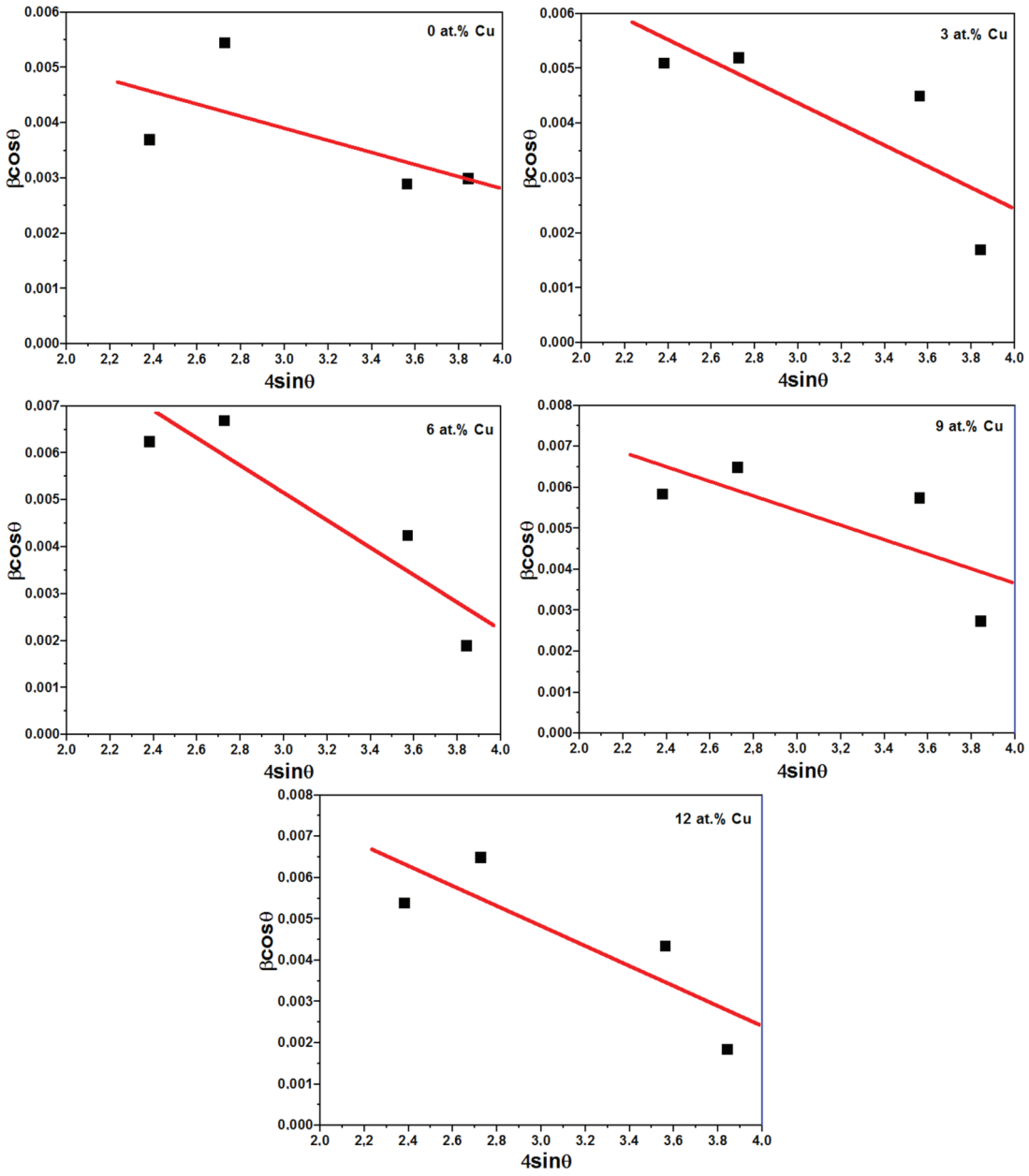

Figure 2. Determination of average crystallite size and microstrain using the Williamson-Hall method

lattice distortion and internal stress. The peak in microstrain and minimum crystallite size at 6 at.% Cu suggest that this concentration corresponds to the highest level of structural disorder, whereas further doping may lead to partial strain relaxation and slight improvement in crystallinity.

3.2. Optical Properties

Figure 4 illustrates the variation of optical transmittance (*T*) as a function of wavelength (300–900 nm) for Cu doped NiO thin films with different copper concentrations (0–12.%). All samples exhibit similar spectral behavior, characterized by low transmittance in the UV region followed by a sharp increase in the visible region and gradual stabilization in the near-infrared region. This trend corresponds to the fundamental absorption edge of NiO. It is clearly observed that Cu doping significantly affects the transmittance of the films. The sample with 3 at.% Cu shows the highest transmittance over the entire wavelength range, indicating improved optical quality. This enhancement may be attributed to better crystallinity and reduced defect density, leading to lower optical losses. In contrast, increasing the Cu concentration beyond 3 at.% (i.e., 6, 9, and 12 at.%) results in

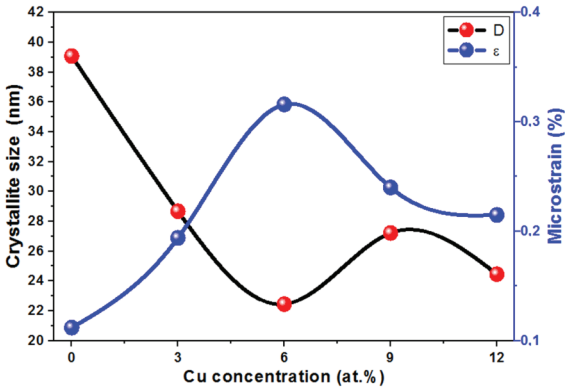

Figure 3. Change in crystallite size D and microstrain ε of Cu doped NiO thin films as a function of copper concentration.

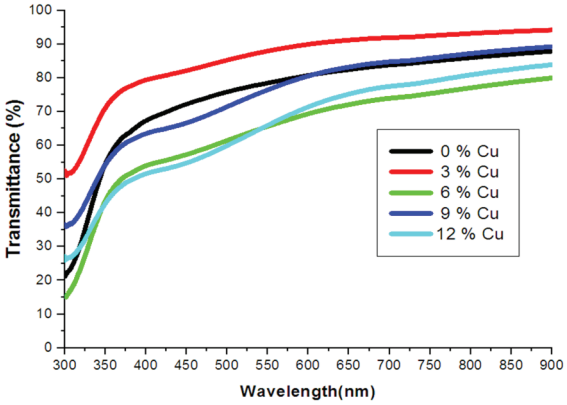

Figure 4. Transmittance (T) as a function of wavelength (λ) of Cu doped NiO thin films at different Cu concentrations.

a gradual decrease in transmittance. This behavior can be explained by the increase in structural defects, impurity scattering, and possible formation of localized states within the band gap, which enhance light absorption. However, a slight shift in the absorption edge can be observed with increasing Cu content, suggesting a modification of the optical band gap. The overall results indicate that moderate Cu doping improves transparency, whereas excessive doping deteriorates the optical performance of NiO thin films.

The absorption coefficient (α) and the incident photon energy ($h\nu$) are related by the following expression [17]:

$$\alpha h\nu = C(h\nu - E_g)^n \qquad (2)$$

where C is a constant, ν is the frequency of the incident radiation, h is the Planck's constant, exponent ν is 1/2 for direct allowed transition (with $h\nu = \dfrac{1240}{\lambda(nm)}$ (eV)), and E_g is the band gap energy of the semiconductor. The band gap energy of the Cu doped NiO films are summarized in Table 2.

For undoped NiO film, the value of E_g is 3.60 eV, which is in good agreement with the value obtained for bulk NiO [18]. It is obvious that the values of E_g decrease with increasing Cu percentage; this change of E_g may be due to the influence of various factors such as film thickness, crystallite size, lattice strain and presence of impurities in the films [19].

The Urbach energy (E_u) describes the exponential tail of localized states within the optical band gap, which is a useful parameter for assessing structural disturbance [20]. The Urbach energy can be calculated using equations (3) and (4). The values of (E_u) were obtained from the reciprocal of the slope of the linear portion of the graph of (lnα) versus ($h\nu$), known as the Urbach coefficient, which was determined using the following relationship [21]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \qquad (3)$$

$$\ln\alpha = \ln\alpha_0 + \frac{1}{E_u}(h\nu) \qquad (4)$$

where (α_0) is the pre-exponential factor, ($h\nu$) the photon energy.

The calculated E_u values range from 0.523 to 0.935 eV and are summarized in Table 2. It can be noted that the Eu values increase with increasing copper doping percentage. The increase in E_u can be attributed to the formation of localized states caused by doping ions in the band gap. Although crystalline defects can contribute to the formation of localized states within the band gap, in this case the effect of copper doping is more significant and dominant.

Figure 5 shows the variation of the optical band gap energy (E_g) and the Urbach energy

Table 2. Variation of band gap energy and Urbach energy values for the Cu doped NiO thin films at different Cu concentrations.

Cu concentrations (at.%)	0	3	6	9	12
Optical band gap energy E_g (eV)	3.6	3.53	3.57	3.46	3.43
Urbach energy E_u (eV)	0.523	0.591	0.644	0.782	0.935

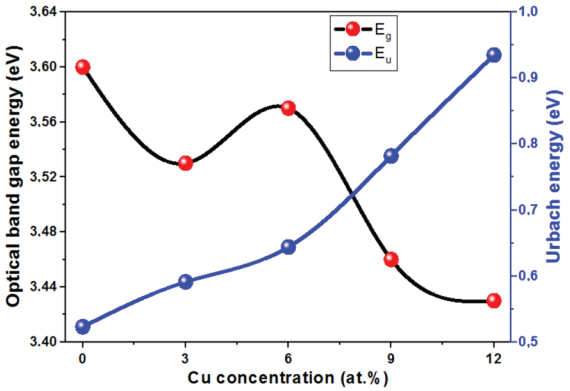

Figure 5. Change in the band gap energy E_g and Urbach energy E_u of copper-doped NiO thin films as a function copper concentration.

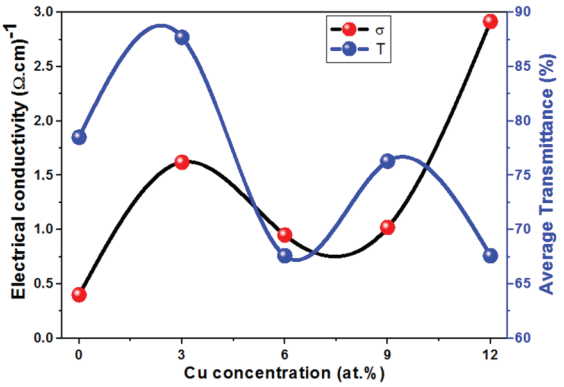

Figure 6. Changes in electrical conductivity and average transmittance of copper-doped NiO thin films as a function of Cu concentration

(E_u) of copper-doped NiO thin films as a function of Cu concentration. The optical band gap decreases from 3.60 eV for the undoped film to 3.43 eV for the film doped with 12 at.% Cu, indicating that Cu incorporation modifies the electronic structure of NiO, despite the reduction in crystallite size and the increase in microstrain observed in Figure 3. This reduction in E_g can be attributed to the formation of impurity levels and defect states within the band gap, which facilitate optical transitions at lower energies. Conversely, the Urbach energy increases from about 0.523 to 0.935 eV with increasing Cu content. The increase in E_u reflects a higher degree of structural disorder and a greater density of localized states near the band edges. The inverse relationship between E_g and E_u suggests that Cu doping enhances band-tail states and lattice imperfections, resulting in a narrowing of the band gap. These findings demonstrate the significant influence of Cu incorporation on the optical properties of NiO thin films.

3.3. Electrical properties

Figure 6 shows the change in electrical conductivity σ and average transmittance of copper-doped NiO thin films as a function of copper concentration. The electrical conductivity and average optical transmittance of copper-doped NiO thin films show a strong dependence on copper concentration. At low doping levels (3 at.%), conductivity increases due to enhanced charge carrier concentration introduced by Cu ions substituting Ni sites. However, at 6 at.%, a slight decrease in conductivity is observed due to increased scattering by defects and structural disturbances. At higher doping (12 at.%), conductivity increases significantly, reaching a recorded value of 2.916 $(\Omega.cm)^{-1}$, indicating improved carrier activation and defect-related conduction pathways. In contrast, optical transmittance exhibits a non-monotonic behavior, increasing at low dopant concentrations and then decreasing at higher concentrations due to enhanced free carrier absorption and defect-induced light scattering effects. Patil et al. [22] have reported that the increase in the electrical conductivity is due to the increase in activation energy with increasing film thickness; this was explained by difference in the experimental conditions of spraying solution, spray rate and cooling of the substrates during decomposition.

4. Conclusion

In conclusion, the spray pyrolysis technique was successfully employed to deposit copper-doped NiO thin films with various Cu concentrations onto glass substrates. All deposited films exhibited a cubic crystal structure with a preferential orientation along the (111) plane. The minimum crystallite size, estimated at 22.45 nm, was obtained at a copper concentration of 6 at.%. An improvement in crystallinity was clearly observed at this doping level, as evidenced by the sharp and intense diffraction peak at $2\theta \approx 37.1$ degrees, corresponding to the (111) plane. This indicates enhanced structural ordering compared to other films. The optical transmittance exhibits a non-monotonic behavior, increasing at low dopant concentrations and then decreasing at higher concentrations due to increased free carrier absorption and defect-induced light scattering effects. The band gap energy decreased from 3.43 to 3.60 eV and the Urbach energy increased from 0.523 to 0.935 eV, as the Cu dopant concentration increased from 0 to 12 at.%. This behavior can be attributed to the formation of impurity levels and defect states within the band gap, which facilitate optical transitions at lower

energies. The electrical conductivity reached 2.916 $(\Omega\ cm)^{-1}$ at 12 at.% Cu, confirming improved charge transport properties. These combined optical and electrical characteristics make copper-doped NiO thin films promising candidates for optoelectronic applications, particularly as window layers in solar cells.

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