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SYNTHESIS AND CHARACTERIZATION OF UN-DOPED AND COPPER DOPED NICKEL OXIDE THIN FILMS

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Article Info	Abstract
Received: 18.03.2024 *Accepted: 08.07.2024* **Keywords:** Thin Films, Metal Oxides, NiO, Pyrolysis spray	In this research, the effect copper on the structural, morphological, optical, and electrical properties of nickel oxide thin films was studied at different copper concentrations. Thin transparent films of nickel oxide (NiO) doped with copper (Cu) were deposited on glass substrates at a temperature of 400 °C using the spray pyrolysis technique. The structural study showed that all the prepared polycrystalline films had a cubic structure with a preferential orientation along (111). Copper was well integrated into the host lattice without changing the structure. SEM images showed that the films were well adhered with a wrinkled network structure. The optical band gap ranges from 3.70 eV to 3.50 eV, and the Urbach energy, which ranges from 0.34 eV to 0.5 eV, has also been discussed. The highest conductivity value of 6.23×10^{-3} $(\Omega\cdot cm)^{-1}$ was found at a copper concentration of 2 %.

1. Introduction

Transparent conducting oxides are materials of great importance in the fields of modern scientific research, science and technology. Transparent conductive oxide films are classified into two types: n and p.

Among the most prominent and best p-type semiconductors, we especially mention Nickel oxide (NiO) because it is an interesting candidate in applications that require p-type semiconductors. All this interest is due to the nanocrystalline NiO films because they have prominent electrical catalytic properties, large optical density, low toxicity, thermal stability, and a range of applications as, for example, electronic devices, car mirrors, heterogeneous solar cells [1] , and energy-saving smart windows.

Nickel oxide (NiO) has a structure similar to cubic rock salt with octahedral Ni^{2+} and O^{2-} positions. The nickel oxide is often asymmetric, which means there is a deviation in the NiO ratio from 1:1 [2]. It has a range of energy gap values from (3.6 - 4eV), and it has been shown that the electrical resistance value is as high as 10^{13} (Ω.cm) of stoichiometry for NiO [3]. NiO nanostructures are manufactured using different techniques such as: Spray pyrolysis [4], Sol-gal process [5], and Pulsed laser deposition [6]. Many studies have shown that the surface morphology and crystal structure depend on the nature and quality of the dopants.

For the purpose of improving the properties of NiO films, many researchers have conducted studies on the effect of dopant on NiO films, for example: Al [7] Fe [8] Cu [9] K [10] Mg [11]. As for thin films of NiO doped with copper (Cu), not much work has been done on them in the past.

2. Experimental details

Thin films of NiO:Cu in different proportions were prepared using the spray pyrolysis technique, as described in [12].

An initial solution was prepared with a concentration of 0.2 mol/L of nickel nitrate hexahydrate ($Ni(NO_3)_2,6H_2O$) in 100 ml distilled water, and for doping with copper, a solution with a concentration of 0.2 mol/L of copper chloride ($CuCl_2,6H_2O$) in 100 ml distilled water was prepared, with drops of hydrochloric acid added to both solutions. The solutions were stirred magnetically for an hour at 60 °C to obtain clear and transparent solutions. The copper solution was added to the nickel solution to obtain atomic ratios of 0, 0.5, 1, 1.5, 2, 3, 4, and 6 % Cu. These thin films were prepared on glass substrates for uniform deposition, and the solution was sprayed through a linearly moving nozzle. The substrate temperature remained constant at 400 °C during film deposition, as this temperature proved ideal for obtaining well-adhesive films. The spray rate was maintained at 1 mL/min using air as the carrier gas, and the distance between the nozzle tip and the substrate was maintained at 24 cm. The films were characterized using various techniques to verify the properties of the composite materials. Structural studies were carried out using a Bruker D8 Advance diffractometer with CuKα radiation (λ= 1.54060Å) to determine the nature of the crystalline phases. SEM and EDS were used to examine the morphological characteristics and determine the chemical composition of the thin films, respectively. Optical properties (transmittance, band gap energy, and Urbach energy) were studied using a UV-Visible spectrophotometer (PerkinElmer Lambda 25) in the wavelength range of 300-900 nm. The electrical properties of the films were measured using the four-probe KEITHLEY 2400 technique.

3. Results and discussion

3.1. Structural properties

Figure 1 shows the XRD patterns of NiO:Cu films, which are thin films that are polycrystalline in nature, where three main diffraction peaks appear for NiO only with (111) (200) (220) placed at 2θ ≈ (37.3 °) (43.3 °) (62.8 °) respectively. All these values agree precisely with the crystal structure of chloride Sodium to nickel, and it agrees well with the standard spectrum (JCPDS, No.47-1049) within the space group (Fm3m) as there are no crystalline phases associated with the dopants even after adding a higher copper content in the nickel films. An increase in the intensity of the peak corresponding to the lattice level (111) corresponding (2 % Cu) was found from copper doping, as this percentage of doping shows an improvement in the peak intensity. This is attributed to the fact that in the case of a decrease in doping, Cu^{2+} ions ($R_{Cu2+} \approx 0.73$ Å) replace Ni^{2+} ions ($R_{Ni2+} \approx 0.69$Å) [13] [14] as a substitute resulting from the relaxing stress. This means better crystallization.

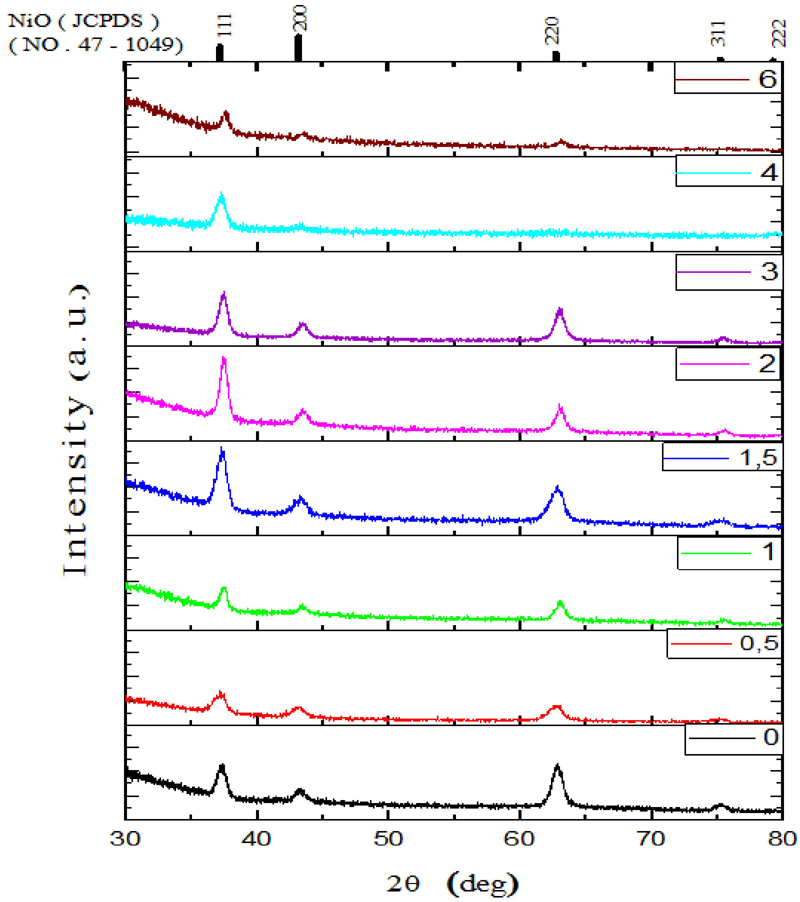

Figure 1. XRD pattern of NiO:Cu thin films

However, when doping was added at a higher percentage, it led to a clear decrease in the peak intensity (111), as this is due to the fact that copper ions may occupy the octahedral sites, which leads to deterioration of crystallinity in the NiO films.

Crystalline size D and microstrain ε were calculated using formulas (1) and (2) [15]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{2}$$

Where λ is the applied X-ray wavelength (0.154060 nm for Cu Kα radiation), β is the full-width at half-maximum (FWHM) in radian and θ is the diffraction peak angle. Table 1 shows the values of crystallite size and strain (ε) for NiO:Cu thin films.

Table 1. Values of crystallites size and strain (ε) of NiO:Cu thin films

Cu concentration (%)	**Thickness (nm)**	**Crystallite size (nm)**	**Microstrain ε × 10^{-3}**
0	142.38	7.45533	4.82173
0.5	175.55	6.09532	5.75317
1	156.67	5.18744	10.85115
1.5	171.91	5.87742	6.48906
2	149.94	8.54603	4.40335
3	158.05	9.82290	3.58577
4	168.80	8.63070	4.01943
6	180.89	3.12782	12.38701

Figure 2 shows the relationship between crystal size D and microstrain ε with different percentages of copper doping. An inverse relationship between crystallite size and microstrain was noted, with crystal size increasing and microstrain decreasing at 1.5, 2, and 3% Cu, indicating improved crystallization due to stress relaxation. Higher doping levels resulted in decreased crystal sizes.

At higher values of doping, a decrease in crystal size values was found, possibly due to copper acting as a stabilizer for crystal growth, while microstrain increased due to structural disorders during the crystal growth process.

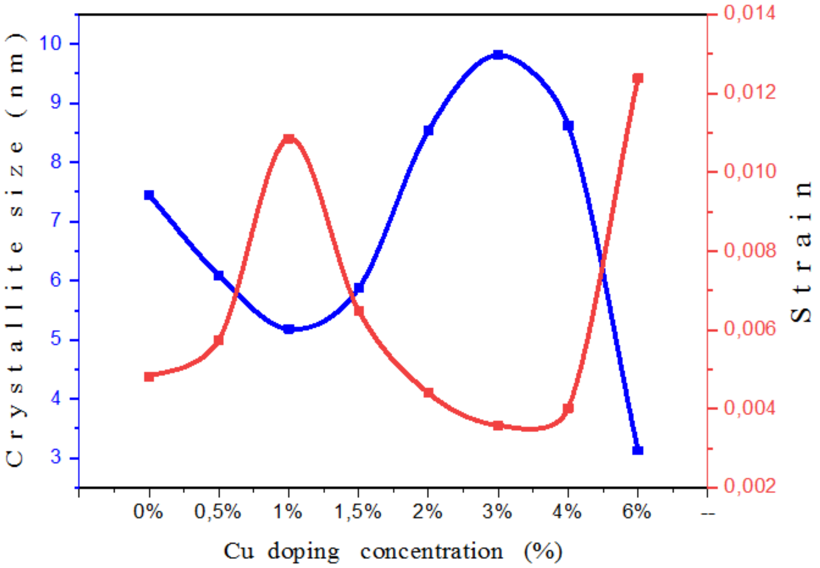

Figure 2. The variation of the crystallite size and strain versus copper concentration

3.2. Morphological study

Figure 3 shows the SEM surface topography of pure NiO films doped with different ratios of Cu (0, 0.5, 1, 1.5, 2, 3, 4, and 6 %). The images show changes in surface topography with varying doping ratios. Pure NiO films exhibit nanoclusters with relatively heterogeneous growth and unclear grain boundaries, but the substrate is well-covered without cracks, forming a wrinkled network structure. Doping with 1 % Cu introduced surface defects, while higher doping levels resulted in spherical particles of regular sizes spread across the substrate, indicating improved surface morphology due to Cu ion incorporation.

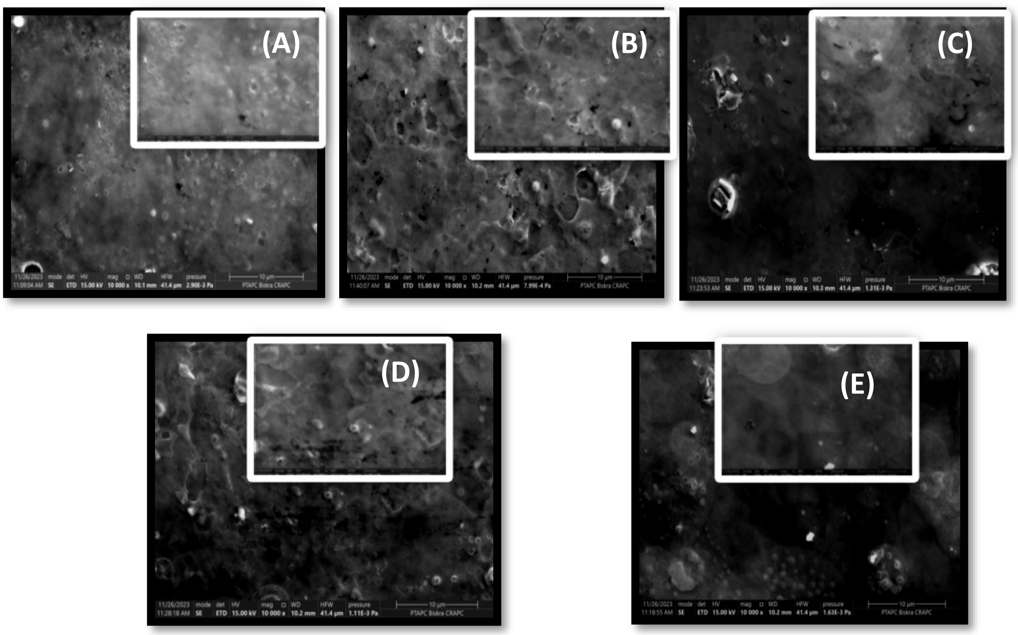

Figure 3. SEM images of Cu-NiO thin films, (A) 0 % Cu , (B) 1 % Cu , (C) 2 % Cu , (D) 4 % Cu and (E) 6 % Cu

3.3. Optical properties

3.3.1. UV–VIS transmittance

An optical study of the NiO:Cu thin films was performed using a spectrophotometer (UV-Vis) at room temperature in transmittance mode. Figure 4 shows the optical transmission spectra of NiO:Cu films in the wavelength region (300-900 nm). The transmittance is low in the ultraviolet region and increases in the visible region, with pure NiO films reaching a transmittance rate of 75.5%. NiO:Cu films with 1-2 % Cu had the best transparency among the samples, surpassing the transmittance of pure NiO. The improved optical transmittance may be due to the changes in particle size. The difference between copper ion radius ($R_{Cu2+} \approx 0.73$ Å) and nickel ion radius ($R_{Ni2+} \approx 0.69$ Å) is due to the difference in roughness that leads to large dispersion and an increase in the band gap. On the other hand, an increase in copper concentration leads to a decrease in transmittance values. This may be due to the large amounts of light that are scattered from the grain boundaries and copper clusters.

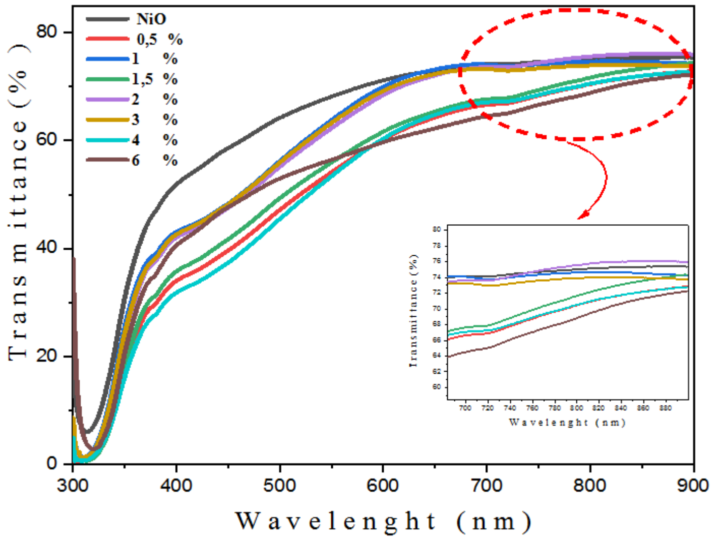

Figure 4. Transmittance of NiO:Cu thin films

3.3.2. Optical band gap

The energy band gap of NiO:Cu films was evaluated according to the Tauc formula (3) [16]:

$$\alpha h\nu = \beta(h\nu - Eg)^m \tag{3}$$

Where the energy band gap values depend on the structural properties of the crystalline films (disorder and regularity) [17]. Returning to the Tauc relationship, we mention that: α is the absorption coefficient $\alpha = \frac{2.303\,A}{t}$, A is the absorbance and t is the film thickness, hν is the photon energy, β is band edge parameter, m values can be 1/2 or 2 for direct and indirect transmission respectively [18] [19]. Literary studies show that NiO is a direct gap material according to some researchers [20] In contrast to others who report that NiO is a direct and indirect gap material [21].

In our current study, direct transformations were considered and studied for NiO:Cu films. A gap was calculated Energy range by extrapolating the linear region of the plots $(\alpha h\nu)^2$ against the energy axis (hν) figure 5. The band gap values for different Cu concentrations are presented in Table 2.

Increased doping concentration led to new donor levels within the band gap, shifting the valence band edge to higher energy and decreasing the band gap values. This also indicates that band gap energy tailing increases with higher doping concentrations. This also means that the effect of tailing on the band gap energy increases with increasing doping concentration [22]. The linear fit of the data points shows that increasing the percentage of copper doping in NiO:Cu films leads to decrease in the optical band gap, as reported by Moghe and all [23]. This decrease in the optical band gap can be attributed to the compressive stress caused by the doping atoms of the lattice [24] .

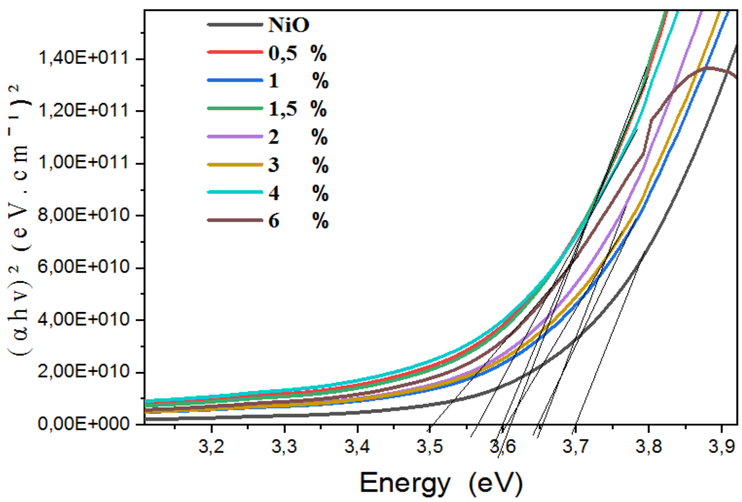

Figure 5. Plot of $(\alpha h\upsilon)^2$ versus incident photon energy hν. Inset shows the variation of optical band gap with Cu %

3.4. Urbach energy

Urbach energy is a measure of the high concentration of defects in the material that distort the band structure in the Tauc region, that is, between the weak absorption tail and the strong absorption peak. Urbach reported that there is a linear relationship between (ln(α)) and (hν) called the Urbach relationship [25]. The Urbach relationship is described by equation (4):

$$\alpha = \alpha_0 \, e^{\frac{h\nu}{Eu}} \tag{4}$$

Where α_0 is the pre-exponential factor, hν is the photon energy, and Eu is the Urbach energy.

The Eu energy is determined from the inverse slope of the linear chart (lnα - hν) as shown in the figure 6, and the values obtained are listed in the table 2, where we notice an increasing proportion between the Urbach energy and the percentage of copper doping. This means that increasing the concentration of doping leads to an increase in the concentration of defects generated in nickel membranes inlaid with copper.

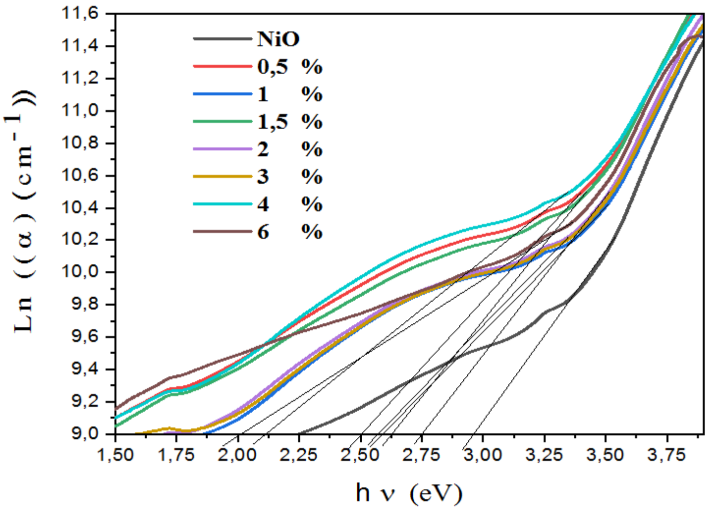

Figure 6. Plot of Ln (α) versus incident photon energy (hν) of Cu-NiO thin films

Figure 7 shows the relationship between the band gap energy and the Urbach energy, where a decrease in the band gap ratio is evident with an increase in the Urbach energy. The same thing was observed by Ali and all [24] .

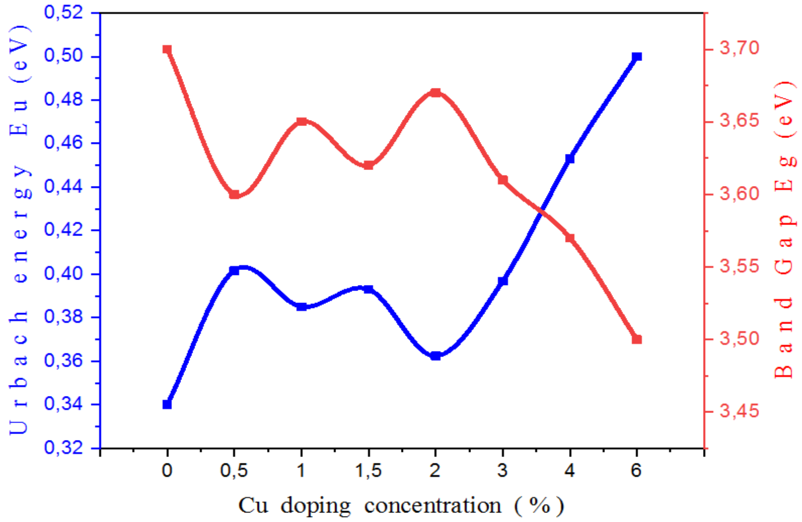

Figure 7. Variation of optical band gap and Urbach energies versus copper concentrations

Table 2. Optical and electrical parameters of NiO:Cu thin films

Cu concentration (%)	**Optical gap energy Eg (eV)**	**Urbach energy Eu (eV)**	**Conductivity σ $(\Omega.cm)^{-1}\times10^{-3}$**
0	3.70	0.3401	3.76
0.5	3.60	0.4017	2.554
1	3.65	0.385	3.7
1.5	3.62	0.393	3.09
2	3.67	0.3624	6.23
3	3.61	0.39685	5.4
4	3.57	0.453	4.93
6	3.50	0.5	3.25

3.5. Electrical properties

The electrical properties of NiO:Cu thin films were studied using the four-point linear probe technique. The conductivity σ of films is determined by the formula (5) [14] :

$$\sigma = \frac{1}{R_{sh} \times d} \tag{5}$$

Where d is the thickness of the film, R_{sh} is the sheet resistance.

The conductivity values are shown in Table 2. Figure 8 shows the connection between conductivity and band tail width of NiO:Cu films as a function of copper content. Since the increase in copper concentration in NiO led to a decrease in electrical resistance, this is due to the generation of holes. Many researchers have reported such a connection [10]. On the other hand, the conductivity increases with the increase in the copper content in nickel oxide films, The highest conductivity $6.23\cdot10^{-3}$ $(\Omega\ cm)^{-1}$ was observed at 2 % Cu. This increase in electrical conductivity is due to the decrease in the width of the tail of the band (Urbach energy), which contributed to the increase in charge movement. At low Cu concentrations, the conduction mechanism involved copper atoms replacing nickel atoms and copper atoms entering NiO interstitial sites. Increasing copper concentrations raised the concentration of acceptor impurities, enhancing conductivity. However, higher doping levels led to impurity ion accumulation, forming deep impurity centers and decreasing conductivity.

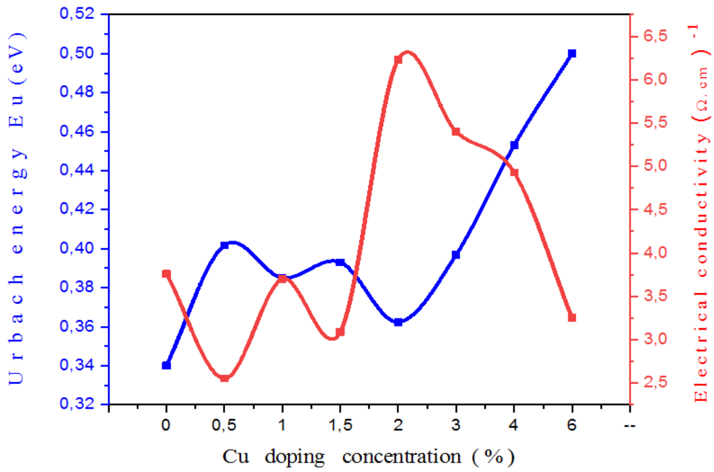

Figure 8. The variation of Urbach energy and electrical conductivity of NiO:Cu thin films

4. Conclusions

NiO:Cu thin films with different copper concentrations (0, 0.5, 1, 1.5, 2, 3, 4, and 6 %) were successfully synthesized on glass substrates at 400 °C using spray pyrolysis. The study revealed significant changes in the structural, optical, and electrical properties of the films with varying copper concentrations. XRD results showed improved crystallization at 2 % Cu doping. The size of the crystals ranged from 3.12 nm to 9.82 nm. SEM images indicated improved surface morphology with higher doping levels. Optical studies showed a decrease in the optical band gap with increasing Cu concentrations, the optical band gap decreased from 3.70 eV to 3.50 eV and electrical studies demonstrated enhanced conductivity at 2 % Cu doping, the highest conductivity is $6.23 \cdot 10^{-3}$ $(\Omega\ \mathrm{cm})^{-1}$. These findings suggest NiO:Cu thin films are suitable for photocatalytic and photovoltaic applications.

References

[1] Chan I.M., Hong F.C., *Improved performance of the single-layer and double-layer organic light emitting diodes by nickel oxide coated indium tin oxide anode*. Thin Solid Films, 450 (2004) 304–11, DOI:10.1016/j.tsf.2003.10.022

[2] Usha K.S., Sivakumar R., Sanjeeviraja C., *Optical constants and dispersion energy*

parameters of NiO thin films prepared by radio frequency magnetron sputtering technique. J. Appl. Phys., 114 (2013) 123501, DOI:10.1063/1.4821966

[3] Adler D., Feinleib J., *Electrical and optical properties of narrow-band materials*. Phys. Rev.B., 2 (1970) 3112–34, DOI:10.1103/PhysRevB.2.3112

[4] Lou X.C., Zhao X.J., Xiong Y.L., Sui X.T.,*The influence of annealing on electrochromic properties of Al-B-NiO thin films prepared by sol-gel*. J. Sol-Gel Sci. Technol., 54 (2010) 43–8, DOI:10.1007/s10971-010-2155-3

[5] Aydin H., Mansour S.A., Aydin C., Al-Ghamdi A.A., Al-Hartomy O.A., El-Tantawy F., Yakuphanoglu F., *Optical properties of nanostructure boron doped NiO thin films*, J. Sol-Gel Sci. Technol., 64 (2012) 728–33, DOI:10.1007/s10971-012-2909-1

[6] Lin Y. Sen, Lin D.J., Chiu L.Y., Lin S.W., *Lithium electrochromism of atmospheric pressure plasma jet-synthesized NiOxCy thin films*. J. Solid State Electrochem. 16 (2012) 2581–90, DOI:10.1007/s10008-012-1664-0

[7] Lou X., Zhao X., Feng J., Zhou X., *Electrochromic properties of Al doped B-subsituted NiO films prepared by sol-gel.* Progress in Organic Coatings, 64 (2009) 300–3, DOI:10.1016/j.porgcoat.2008.09.006

[8] Godbole B., Badera N., Shrivastava S.B., Jain D., Ganesan V., *Investigation of Fe-doped and -undoped NiO nanocrystalline films*. Surf. Rev. Lett., 14 (2007) 1113–9,

[9] Ben Amor M., Boukhachem A., Boubaker K., Amlouk M., *Structural, optical and electrical studies on Mg-doped NiO thin films for sensitivity applications*. Mater Sci. Semicond. Process, 27 (2014) 994–1006. DOI:10.1016/j.mssp.2014.08.008

[10] Chen S.C., Kuo T.Y., Lin Y.C., Lin H.C., *Preparation and properties of p-type transparent conductive Cu-doped NiO films*. Thin Solid Films, 519 (2011) 4944–7, DOI:10.1016/j.tsf.2011.01.058

[11] Aftab M., Butt M.Z., Ali D., Bashir F., Aftab Z.H., *Corrigendum to "Impact of copper doping in NiO thin films on their structure, morphology, and antibacterial activity against Escherichia Coli.",* Ceram. Int., 46 (2020) 5037-5049, DOI:10.1016/j.ceramint.2020.11.178

[12] Patil P.S., *Versatility of chemical spray pyrolysis technique*. Mater Chem. Phys., 59 (1999) 185–98, DOI:10.1016/S0254-0584(99)00049-8

[13] Ghougali M., Belahssen O., Chala A., *Effect of annealing in physical properties of NiO nanostructure thin film*. J. Nano- Electron Phys., 9 (2017) 1–3, DOI: 10.21272/jnep.9(3).03043

[14] Ghougali M., Belahssen O., Benhamida S., Mimouni M., Rihia G., Mahboub M.S.,

Beggas A., *Investigation of the physical properties of nanostructured Co:NiO thin films*. Chalcogenide Lett., 18 (2021) 765–75, DOI: 10.15251/CL.2021.1812.765

[15] Mrabet C., Ben Amor M., Boukhachem A., Amlouk M., Manoubi T., *Physical properties of La-doped NiO sprayed thin films for optoelectronic and sensor applications*. Ceram. Int., 42 (2016) 5963–78, DOI: 10.1016/j.ceramint.2015.12.144

[16] Tauc J., *Absorption edge and internal electric fields in amorphous semiconductors*. Mater Res. Bull. 5 (1970) 721–9, DOI :10.1016/0025-5408(70)90112-1

[17] Armenise M.N., Campanella C.E., Ciminelli C., Dell'Olio F., Passaro V.M.N., *Phononic and photonic band gap structures: Modelling and applications*. Phys. Procedia, 3 (2010) 357–64, DOI: 10.1016/j.phpro.2010.01.047

[18] Asaithambi S., Sakthivel P., Karuppaiah M., Yuvakkumar R., Balamurugan K., Ahamad T., Khan M.A.M., Ramalingam G., Mohammed M.K.A., Ravi G., *Preparation of Fe-SnO2@CeO2 nanocomposite electrode for asymmetric supercapacitor device performance analysis*. J. Energy Storage, 36 (2021) DOI: 10.1016/j.est.2021.102402 .

[19] Banu Bahşi Z., Oral A.Y., *Effects of Mn and Cu doping on the microstructures and optical properties of sol-gel derived ZnO thin films*. Opt. Mater, 29 (2007) 672–8. DOI:10.1016/j.optmat.2005.11.016

[20] Turgut G., Sonmez E., Duman S., *Determination of certain sol-gel growth parameters of nickel oxide films*. Ceram. Int., 41 (2015) 2976–89, DOI:10.1016/j.ceramint.2014.10.133

[21] Paul Joseph D., Saravanan M., Muthuraaman B., Renugambal P., Sambasivam S., Philip Raja S., Maruthamuthu P., Venkateswaran C., *Spray deposition and characterization of nanostructured Li doped NiO thin films for application in dye-sensitized solar cells*. Nanotechnology, 19 (2008) DOI:10.1088/0957-4484/19/48/485707

[22] Ikhmayies S.J., Ahmad-Bitar R.N., *A study of the optical bandgap energy and Urbach tail of spray-deposited CdS:In thin films*. J. Mater Res. Technol., Korea Institute of Oriental Medicine,; 2 (2013) 221–7, DOI: 10.1016/j.jmrt.2013.02.012

[23] Moghe S., Acharya A.D., Panda R., Shrivastava S.B., Gangrade M., Shripathi T., Ganesan V., *Effect of copper doping on the change in the optical absorption behaviour in NiO thin films*. Renew Energy, 46 (2012) 43–8, DOI: 10.1016/j.renene.2012.02.028.

[24] Ali D., Butt M.Z., Arif B., Al-Ghamdi A.A., Yakuphanoglu F., *The role of Al, Ba, and Cd dopant elements in tailoring the properties of c-axis oriented ZnO thin films*. Phys. B Condens. Matter, 506 (2017) 83–93, DOI: 10.1016/j.physb.2016.11.003

[25] Urbach F., *The long-wavelength edge of photographic sensitivity and of the electronic Absorption of Solids*, . Phys Rev., 92 (1953) 1324, DOI: 10.1103/PhysRev.92.1324