Effect of Co-doping on Structural, Morphological, Optical and Electrical Properties of *p*-type CuO Films

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In the present work, we studied the effect of cobalt (Co) doping rate between 2 % and 6 % on the structural, optical and electrical properties of thin films from copper acetate (Cu(CH₃COO)₂·H₂O) produced by spray pyrolysis. The results obtained during the various characterizations carried out (Raman, contact angle, UV-Visible and the Hall effect) show that our films have a monoclinic structure with the presence of a single CuO phase. The measured contact angles are less than 90° for the CuO undoped, CuO:2 %Co and CuO:4 % Co confirming the hydrophilic character of the films, as well as the 6 % doped film shows the hydrophobic character with a contact angle greater than 90° ($\theta = 97.41°$). An improvement of the absorption by the reduction of the transmittance for the films doped with 2 % Co, 4 % Co and 6 % Co with a low value of the transmission obtained in this work for the CuO:6 % Co film equal to 7.34 %. A decrease in the values of the optical gap as a function of cobalt doping with a low value equal to 1.66 eV found for the thin layer of CuO:6 % Co. The electrical analysis shows that the conductivity increases with the addition of cobalt to the CuO with a high value for the film doped with 6 % ($\sigma = 7.246 \times 10^{-1}$ (Ω·cm)$^{-1}$). So, CuO-doped 6% cobalt has good physical characteristics which allow it to be used as a layer absorbing solar radiation in thin-film solar cells.

Keywords: *p*-type CuO, Co-doping, Spray pyrolysis, Raman, Contact angle.

1. INTRODUCTION

Nanocrystalline oxide semiconductors of *n*-type, such as ZnO, SnO₂, TiO₂,…, and *p*-type, such as NiO, CuO, Cu₂O, Co₃O₄,… with a narrow bandgap have been widely studied for their potential applications in various energy and environmental sectors [1-3]. Among these, during this work, we were more specifically interested in cupric oxide (CuO) which is currently one of the most promising *p*-type semiconductors for applications in solar cells due to their chemical inertness, their non-toxicity, their low cost compared to other metals and their higher optical absorption. The bandgap is around 1.5 eV, which is very close to the ideal bandgap of 1.4 eV for photovoltaic (PV) devices and considered a splendid absorber of sunlight [4]. Thanks to numerous studies carried out in recent years, thin layers of CuO have been prepared by physical and chemical methods. These studies examined the influence of different parameters such as deposition temperature, annealing temperature, atomizer-substrate distance, precursor molarity, solvent properties and deposition time. Considering that the introduction of impurities can effectively modify the physical properties of the resulting thin films, researchers were encouraged to optimize the characteristics of CuO films by using an appropriate dopant. So the doping of CuO with different transition metals such as Mn, Fe, Zn, etc. is also an effective strategy to improve the properties of PV devices. Uddin et al. [5] deposited thin layers of Ni-doped CuO using the spray pyrolysis method and modified the morphological, structural, optical and electrical properties of the films. Gnanasekar et al. [6] used La to improve the photo-current properties of CuO thin films deposited by

spray pyrolysis for photo-sensor applications. Baturay et al. [7] observed the effect of Co doping on electrical and optical properties of CuO films using a spin coating technique. These different intriguing results triggered our interest in this particular material CuO seeing that the nanocrystalline play a vital role to determine the crucial properties of the material for any suitable device applications.

In this work, pure, cobalt (Co)-doped CuO nanocrystals were synthesized using a simple chemical method of spray pyrolysis and fully characterized. In addition, our study also consists in studying the effect of cobalt doping for different concentrations 2 %, 4 % and 6 % on the structural, optical and electrical properties of CuO in order to improve the efficiency of solar cells.

2. EXPERIMENTAL DETAILS

In our study we prepared our films for different doping levels (2 % Co, 4 % Co and 6 % Co), the solution of which was prepared from a mixture of copper acetate (Cu(CH₃COO)₂·H₂O) of mass 2.2 g and methanol (CH₃OH) with a source of cobalt (CoCl₂H₂O) and the other parameters are fixed, such as the molarity equal to 0.2 mol/litre and the deposition time equal to 25 min (Table 1).

Films structural properties were determined by the micro-Raman measurements were performed at room temperature using the 633 nm line of an argon ion laser as the excitation source (Renishaw). Contact angle measurements were carried out at room temperature using an optical system composed of a lamp delivering white light and projecting the image of the drop deposited on the sample (LEYBOLD type light source (6 V, 30 W)).

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**Table 1** – The conditions of the experimental repository

Repository settings	Deposit conditions
Technical	Pyrolysis spray
Precursors	$Cu(CH_3COO)_2 \cdot H_2O$ CH_3OH $CoCl_2H_2O$
Substrate	Ordinary glass
Substrate temperature	400 °C
Solution flow	2 ml/min
Air flow	3 bar
Distance substrate holder-atomizer	25 cm

The optical properties were studied using Shimadzu, model UV-3101PC UV–Vis-NIR spectrophotometer in the wavelength range of 300-800 nm. The electrical properties of the prepared films were examined using a van der Pauw configured Hall measurement system (Ecopia HMS 3000 Hall Measurement System) at room temperatur.

3. RESULTS AND DISCUSSION

3.1 Raman Spectroscopy Study

Using a Raman spectroscopy, the structure of undoped and cobalt-doped CuO thin films at a substrate temperature = 400 °C produced by spray pyrolysis was examined. All tests were performed with a 633 nm laser source at room temperature. The spectra obtained are grouped together in Fig. 1 below.
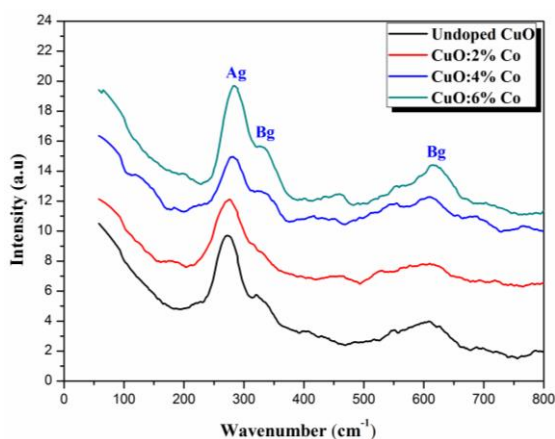

Fig. 1 – Raman spectra of undoped and Co-doped (2 %, 4 % and 6 %) CuO thin films

Fig. 1 shows the Raman spectra of CuO thin films, CuO:2 % Co, CuO:4 % Co and CuO:6 % Co. The Raman spectrum of each film produced by spray pyrolysis is composed of three main phonon modes (Ag and 2Bg) located at 276.43, 322.63 and 601.43 cm^{-1}. These peaks are widely reported in the literature [8-9]. This confirms the presence of a single CuO phase with a monoclinic structure [8-10].

In Fig. 2 we have reported the variation of the intensity of the Raman modes as a function of the cobalt concentration. In the studied doping range, the intensity of the three Raman modes increases with the addition of Co. This can be attributed to the increase in the

thickness of the films with the addition of CuO doping. Lamri Zeggar et al. [8] studied the variation of Raman modes in thin layers of CuO produced by the spray pyrolysis method as a function of thickness using Raman spectroscopy. They noted that the increase in thickness leads to an increase in the intensity of the main Raman modes.
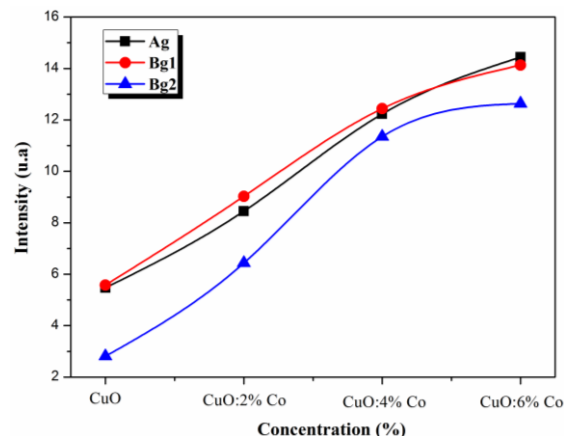
**Fig. 2** – Variation of the intensity of the three Raman modes of our processed films
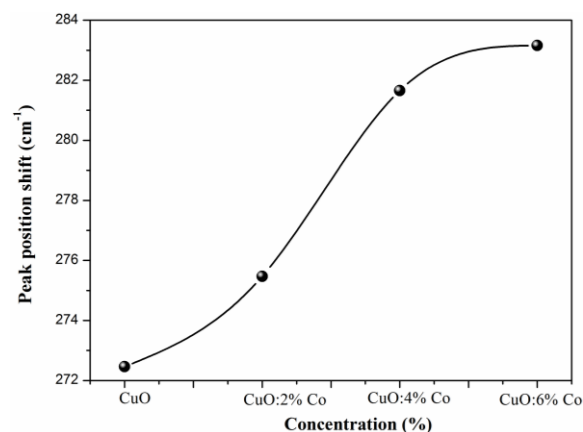
Fig. 3 – Variation in peak position shift for undoped and Co-doped CuO films

In Fig. 3, we have reported the displacement of the Ag mode peak position as a function of cobalt doping. We can notice according to Fig. 3, that the Ag peak moves towards low frequencies (redshift) with the addition of cobalt concentrations between 0 % up to 6 % to copper oxide (CuO). The same variation is observed by Swamy et al. [11]. They found an increase in redshift for Raman Ag mode, with a decrease in crystallite size (D) from 23 to 5 nm for tin oxide nanocrystallite (TiO_2). Decreasing crystallite size causes wavenumber shift and broadening of Raman peaks due to phonon confinement. This has been observed for many semiconductor materials and small oxides such as: $(MnZn)F_2$ and TiO_2 [12-13]. Moreover, the shift of the peaks can be explained by the change in morphology of the CuO films after doping with Co ions [10].

3.2 Wettability Study

Static contact angle (CA, θ) measurements were

made on the surfaces of undoped and Co-doped CuO films on ordinary glass substrate for room temperature (27 °C) and constant humidity (27 RH %). In order to reduce as much as possible the evaporation of the drop of distilled water, all CA measurements are made after 5 seconds for a volume equal to 5 µl deposited using a micropipette. Images of the drop are captured by a video camera (Fig. 4). To give meaning to our measurement, we take the average of five (05) values of the θ of the drop of water at different places on the surface for each film.
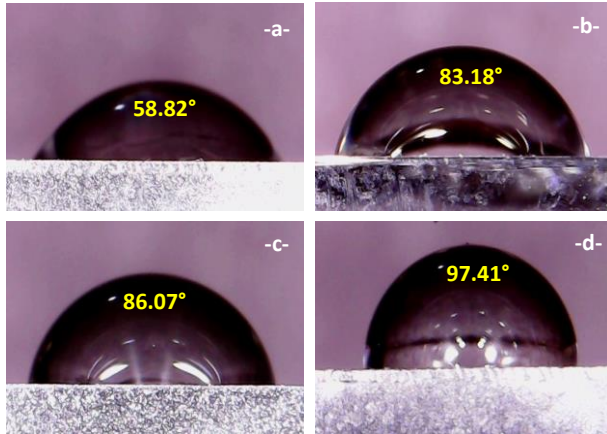

Fig. 4 – Water contact angle images of undoped and Co doped CuO samples

The images of the contact angle of the water drop on the surface of the undoped and Co-doped CuO films are shown in Fig. 4. An increase in the contact angle to 58.82°, 83.18°, 86.07° and 97.41° for concentrations of 0 %, 2 %, 4 % and 6 %, respectively. The experimentally measured contact angle values of pure CuO films, CuO:2 % C and CuO:4 % Co are less than 90° written hydrophilicity character, on the one hand. On the other hand, the contact angle is > 90° for the 6 % Co doped film which shows the hydrophobic character. This character presents an important characteristic for solar cells. The variation of the contact angle as a function of cobalt doping is probably due to the size of the pores available, the radius of the pores and/or their distribution [14], the density of the layers, the deposition technique and crystallite size [15-17]. From these results, the 4 % doping concentration can be regarded as a critical concentration in the change of the surface morphology by the hydrophilic character towards the hydrophobic character of Co-doped CuO. The same behavior was observed by Guermat et al. [18] by studying the effect of Zn on the structural, morphological, optical and electrical properties of SnO$_2$ films elaborated by spray pyrolysis which is related to changes in surface roughness in the crystallization process.

3.3 Optical Study

In order to study the influence of Co doping on the optical properties, the transmittance of prepared CuO thin films were recorded in the range of 400-900 nm (Fig. 5).

All the resulting thin films showed strong absorption in the visible region (400-600 nm), which gradually decreased in the infrared region. As the Co concentration
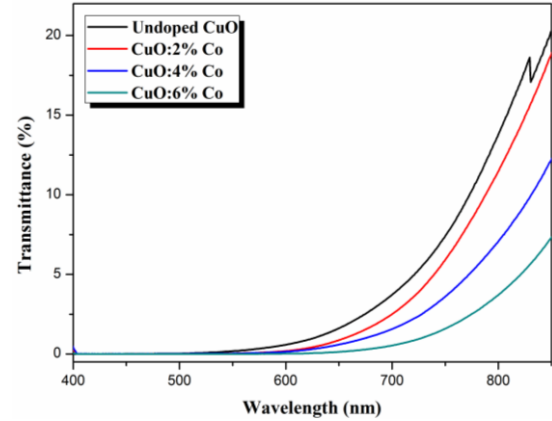
Fig. 5 – Optical transmission spectra of undoped and Co doped CuO films (2 %, 4 % and 6 %)

increases, the absorption in the visible region (the high absorption region) decreases slightly, while the films exhibit more absorption in the near infrared region (the low absorption region). According to the results of Table 1, the increase in the Co doping leads to an increase in the thickness. Therefore, a reduction in absorption in the visible region for CuO thin films can be logically expected. Moreover, it is well confirmed that the absorption in the low absorption region is the result of defects and impurities, which can adequately explain the increase in absorption in the near-infrared region with the increased Co incorporation. The same behavior has been observed by other studies [19-20]. Nevertheless, the result demonstrates that cobalt-doped copper oxide was feasible for direct absorption of solar radiation in thin-film solar cells.

Table 1 – Maximum transmission values for $\lambda = 900$ nm of thin films based on undoped and doped CuO (2 % Co, 4 % Co and 6 % Co)

| Sample	Max. T for $\lambda = 900$ nm, (%)	Thickness, (nm)
100 % CuO	20.21	437
CuO :2 %Co	18.87	501
CuO :4 %Co	13.45	542
CuO :6 %Co	7.34	559

The optical gap value (band gap, E_g) of undoped and cobalt-doped CuO thin films is an important parameter for estimating the absorption band limit of thin films. For this, we estimated the optical gap (E_g) of our films from the transmittance spectra following the Tauc model in high absorption [15].
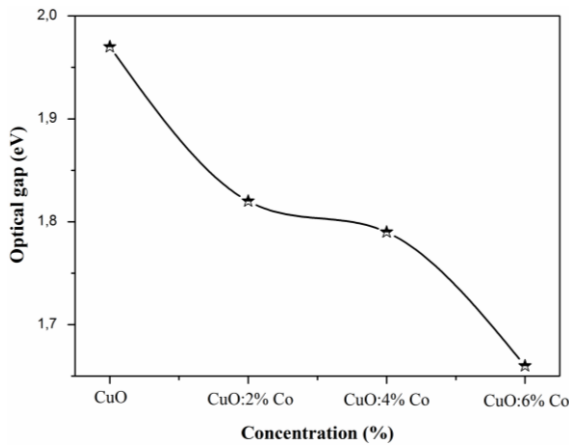
$$(\alpha h v) = A(h v - E_g)^n, \qquad (1)$$

where A is a constant and n is an index which characterizes the type of optical absorption.

With $n = 1/2$ for direct transitions and $n = 2$ for indirect transitions [3]. The bandgap energies are then obtained by extrapolating the linear part of the graphs $(\alpha h v)^2$ as a function of ($h v$) to the energy axis at $(\alpha h v)^2 = 0$ as shown in Fig. 6.

Fig. 7 represents the variation of the optical gap (E_g) of our films. According to Fig. 7, the value of E_g decreases with Co doping. This decrease in the gap with the doping rate is essentially due to the distortions
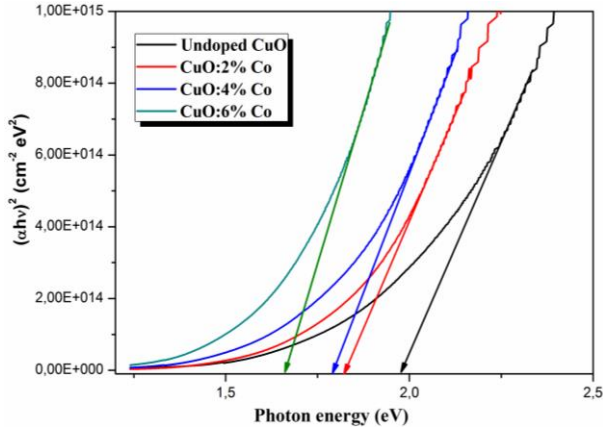
Fig. 6 – Determination of the energy gap by the extrapolation method from the variation $(\alpha h v)^2$ as a function of $(h v)$ for CuO doped with different concentrations of Co
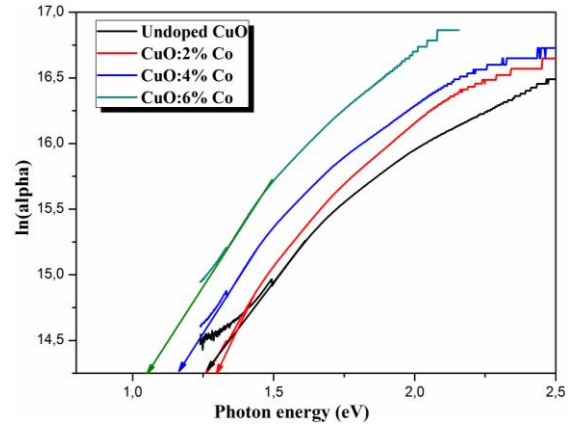

Fig. 8 – Determination of disorder by extrapolation from the variation of $\ln(\alpha)$ as a function of $h v$

Fig. 7 – Variation of the optical gap for %Co-doped CuO thin films

Fig. 9 – Variation of the Urbach energy of our films

caused in the lattice, following the introduction of impurity (doping) which led to the creation of the energy levels inside the band gap of the elaborate films. Moreover, the reduction of the optical gap is seen during the insertion of Co in the matrix of CuO, this can be due to the disorder generated by the defects and the electronic impurities in the matrix [21]. However, Dutta et al. [22] consider that the decrease in the band gap can be related to the decreasing trend of the deformation, where the latter changes the interatomic spacing of the semiconductors which affects the gap energy.
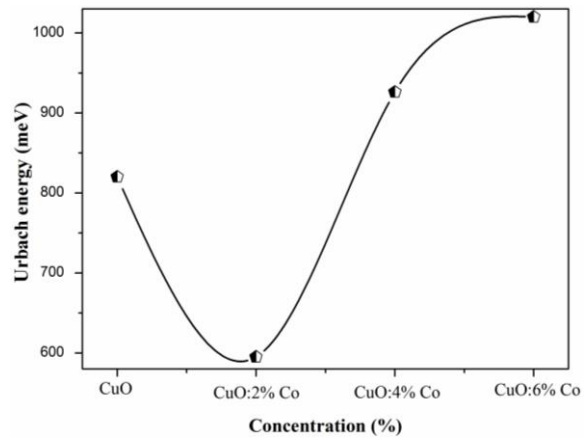
The Urbach energy (disorder, E_U) gives the extent of the tail of localized states in the optical band space, which has been considered a useful parameter to assess the degree of structural disorder [15]. Therefore, one can calculate the Urbach energy of thin layers of undoped and cobalt-doped copper oxide from Urbach's law by the track the $\ln(\alpha)$ in terms of $(h v)$ as mentioned in Fig. 8.

Fig. 9 shows the disorder evolution of copper oxide (CuO) films as a function of Co content. According to Fig. 9, we notice a decrease in disorder with the introduction of dopant in 2 % cobalt in the CuO lattice, on the one hand.

On the other hand, beyond 2 % Co up to 6 % Co we observe an increase for the Urbach energy.

The refractive index (n) is very important in determining the optical properties of semiconductors, knowledge of the latter is essential in the design of hetero-structures of lasers as well as in optoelectronic devices. From the transmission spectra obtained for the undoped and cobalt-doped CuO films, the refractive index can be determined. The refractive index of the film can be calculated using the relationship of Herve and Vandamme [23]:

$$n = \sqrt{1 + \left(\frac{A}{Eg + B}\right)^2} \qquad (2)$$

where A and B are numerical constants with values of 13.6 eV and 3.4 eV, respectively. The variation of refractive index (n) of film is shown in Table 2.

Table 2 – The values of the refractive index (n) and contact angle (CA) of our films

Sample	Refractive index	Cantact angle, (°)
100% CuO	2.722	58.82
CuO:2 % Co	2.790	83.18°
CuO:4 % Co	2.804	86.07°
CuO:6 % Co	2.867	97.41

From Table 2 we notice that the values of the refrac-tive index (n) are between 2.722 and 2.867, since n is strongly related to the forbidden energy band, we can observe also that the layer that presents the smallest

band forbidden has a higher refractive index value. Moreover, the evolution of the refractive index is similar to that of the contact angle (Table 2). This result confirms the hydrophobic character obtained for CuO:6 % Co (Fig. 4) by the densification of this film.

Electrical resistivity (ρ) was characterized using Hall effect measurements to determine the concentration (n) and mobility of charge carriers (μ). In Fig. 10 we have shown the variation of resistivity, charge carrier mobility and charge carrier concentration of pure and Co-doped CuO films. As can be seen, the electrical resistivity decreases as a function of cobalt concentration with a decrease in mobility for the 2 % Co doped film then increases for the 4 % Co and 6 % Co doped films. In the range of cobalt concentration studied (2 % up to 6 %), the resistivity varies between 455.8 up to 1.38 Ω·cm. This indicates that molarity affects electrical transport in CuO thin films. We also note that the concentration of charge carriers goes from 1.857×10^{12} to 1.582×10^{17} cm^{-3}. The same observation was found by Haque Babu et al. [20]. Moreover, the value of the resistivity found in this work for the CuO:6 % Co film ($\rho = 1.38$ Ω·cm) produced by spray pyrolysis is high compared to that obtained ($\rho = 361.4$ Ω·cm) by the spin coating technique [7].
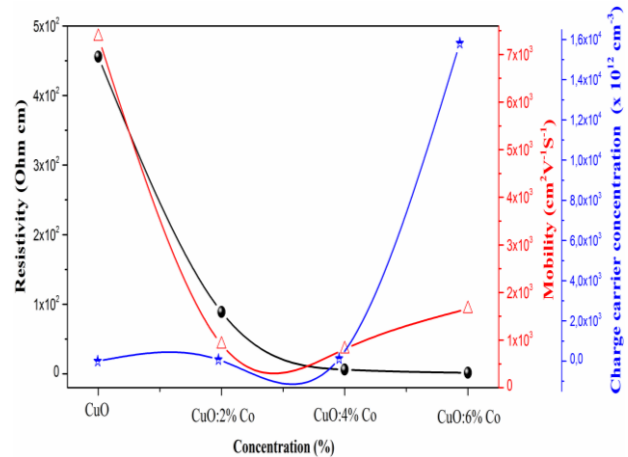
It is well known that the conductivity of a semiconductor can be expressed by:

$$\sigma = n \times \mu \times q. \tag{3}$$

Where n is the concentration of free carriers, μ is the mobility and q is the elementary electronic charge. According to this equation, the electrical conductivity (σ) in the semiconductor is proportional to the product of the carrier concentration and the mobility. Increasing these two parameters (n and μ) improves the conductivity in the films. As can be seen, the electrical conductivity faithfully follows the evolution of the carrier concentration. This clearly indicates that the conductivity is rather controlled by the concentration of the charge carriers than by their mobility [24]. Thus, these cobalt-deposited copper oxide thin films have feasible application in the fabrication of *p-n* junction devices.

Fig. 10 – Variation of resistivity (ρ), charge carrier mobility (μ) and charge carrier concentration (n) of pure and Co-doped CuO films

4. CONCLUSION

In the current study, we presented the results found based on films of pure copper oxide (CuO), doped with cobalt (2 %, 4 % and 6 %) produced by the spray pyrolysis technique, after we characterized these structurally, morphological, optically and electrically. Raman analysis confirmed that the deposited thin layers have a monoclinic structure. The measured contact angle values of the pure CuO films, CuO:2 % Co and CuO:4 % Co are less than 90° describe hydrophilicity character, as well as, the contact angle is > 90° for the 6 % Co doped film which shows the hydrophobic character who is important characteristic for solar cells. The electrical characterization shows that the cobalt doping realised by spray pyrolysis improves the electrical conductivity by decreasing the resistivity from 455.8 Ω·cm for the undoped CuO film to 1.38 Ω·cm for the CuO:6 % Co film.

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Вплив спільного легування на структурні, морфологічні, оптичні та електричні властивості плівок CuO

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У даній роботі був досліджений вплив легування кобальтом (Co) від 2 до 6 % на структурні, оптичні та електричні властивості тонких плівок ацетату міді (Cu(CH₃COO)₂·H₂O), отриманих розпиленням. піроліз. Результати, отримані під час різних проведених характеристик (комбінаційного розсіювання, контактного кута, УФ-видимого та ефекту Холла), показують, що наші плівки мають моноклінну структуру з присутністю однієї фази CuO. Виміряні контактні кути становлять менше 90° для нелегованої CuO, CuO:2 %Co та CuO:4 %Co, що підтверджує гідрофільний характер плівок, а також плівка, легована 6 %, демонструє гідрофобний характер із контактним кутом понад 90° ($\theta = 97.41°$). Поліпшення поглинання шляхом зменшення коефіцієнта пропускання для плівок, легованих 2 % Co, 4 % Co та 6 % Co, з низьким значенням пропускання, отриманим у цій роботі для плівки CuO:6 % Co, рівним 7,34 %. Зменшення значень оптичної щілини як функції легування кобальтом з низьким значенням, рівним 1,66 еВ, виявлено для тонкого шару CuO:6 % Co. Електричний аналіз показує, що провідність збільшується з додаванням кобальту до CuO з високим значенням для плівки, легованої 6 % ($\sigma = 7.246 \times 10^{-1}$ (Ω·cm)$^{-1}$). Так, 6% кобальт, легований CuO, має хороші фізичні характеристики, які дозволяють використовувати його як шар, що поглинає сонячне випромінювання, в тонкоплівкових сонячних елементах.

Ключові слова: CuO *p*-типу, Легування, Піроліз розпиленням, Комбінаційне розсіювання, Контактний кут.