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Structural, optical and electrical properties of copper oxide thin films deposited by spray pyrolysis

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In this work, we have developed thin layers of CuO by method of pyrolysis spray. The samples developed are obtained from the use of copper chloride precursor $CuCl_2$ with molarity of 0.1 mol/l and a spray number that varies between 25 to 150 spray with a step of 25 spray to see the effect of this parameter on the structural, optical and electrical properties of our material. The structural characterization of the obtained thin layers was done by X-ray diffraction (XDR) and spectroscopy Raman. The optical characterization was done by UV visible spectroscopy and electrical characterization by four points. The XDR has confirmed the crystalline state of our thin layers and the formation of the CuO with a preferential direction according to the plan (002). The Raman spectroscopy allowed us to confirm the presence of a thin layer based on the CuO. The lattice parameters remain mainly constant. The spectra UV visible of films has given a transmission varies between 80% and 40% in visible. The optical gap determined varies between 1.75 eV and 1.2 eV. Electrical characterization shows that the resistivity varied between 3.21KΩ.cm and 1.7KΩ.cm depending on number of spray for ethanol gas sensing applications.

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Keywords: Copper oxide, Films, XDR, Spectroscopy Raman, Optical properties, Electrical properties, Spray pyrolysis, Solar cells

1. Introduction

Among metal oxides, copper oxide (CuO) has gained a leading edge in most technological applications. This material receives special attention in various fields of research and industries because of its appropriate range of applications. In addition, CuO has been the subject of several studies because of its interesting properties as a type p semiconductor with an optical gap equal to or greater than 1.2 eV [1], simplicity of preparation, abundant in nature, low cost and non-toxic. This material is considered today as one of the most used in photovoltaic module technologies for the manufacture of solar cells, because of its high solar absorption, low thermal emission, good electrical properties and high carrier concentration. This material is also promising as an electrode material for the next generation of rechargeable lithium batteries, due to its high theoretical capacity, its safety towards the environment. It is also widely used in gas sensors. As a result, demand for CuO is expected to increase rapidly due to its high quality and unique crystalline phase. Therefore, this material has been studied to be considered a future material because of its encouraging properties in various other applications including energy materials [2], supercapacitors [3], magnetic storage [4], photodetectors [5], spintronics and superconductors [6, 7], photocatalysis[8], nanofluids and heat transfer applications [9], biosensors [10, 11], and elimination of inorganic pollutants [12]. Based on these considerations, CuO nanostructures also have more attractive magnetic properties. The physical properties of copper oxide are strongly related to the preparation methods. There is a wide variety of techniques for developing thin layers of the CuO. Examples electro deposition [13], laser ablation [14],and thermal oxidation [15]

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and spray pyrolysis [16]. Among these techniques, spray pyrolysis was used for the development of our thin layers of copper oxide. This technique is certainly interesting; it is a simple technique and allows producing materials of a very high purity. The opto-electric properties will be studied according to the number of sprays for possible application in solar cells and gas sensors [17].

In our work we will present the influence of spray number on improving of the structural properties, optical and electrical thin layers of copper oxide CuO that are deposited on a substrate of glass heated to a temperature of 350 °C by the pyrolysis spray method with a spray number that varies between 25 and 150 spray with a 25 spray step and using the 0.1 M molar copper chloride solution For ethanol gas sensor applications.

2. Preparation method

CuO copper oxide films were obtained from $CuCl_2$ copper chlorides with a molarity of 0.1 M, our 1*1 cm^2 glass substrates were heated to a temperature of 350 ^{0}C.

The film thickness was measured using a Profilometer, where a diamond stylus passes through the sample from the substrate on the oxide film, the crystalline structure was evaluated using a Philips X'Pert diffractometer with $CuK\alpha_1$ radiation ($\lambda = 1.54$ A^0), the latter scans between 20^0 and 70^0. Our Raman spectra were recorded using a spectrometer Raman Bruker will smell with an AlGaAs excitation to Laser 532 nm. The optical transmission and reflection spectra were recorded with UV-Visible in the 200-900 nm wavelength range. Electrical resistivity was measured with the four points.

3. Materials and methods

CuO will be deposited on glass substrates that are cut by a diamond-tipped pen. Taking into account that the quality of the deposit depends on the purity and the surface condition of the substrate, the latter are treated with acetone, after rinsing with distilled water and finally drying with a dryer.

To obtain the oxide films of copper CuO, we sprayed a solution of copper chloride $CuCl_2$ on a glass substrate heated to 350°C. This temperature causes the following reaction:

$$CuCl_2+H_2O \xrightarrow[\text{air}]{T=350°C} CuO+2HCl$$

4. Results and discussions

4.1. Structural characterization

Figure 1 Shows the diffraction spectra of the CuO thin films obtained for a spray number of 25, 50, 75, 100, 125 and 150 spray. According to JCPDS n°. 45-0937.The diffraction spectra on the diagrams show that our material has a polycrystalline structure. The diffractgrams show prominent (002) atomic planes located at 2θ values of 35.5° for all the prepared films at various number spray. The CuO phase has also been reported in various studies [18-20], where (002) preferential orientation is observed. Kose et al. [21] observed that plan (-111) is a preferential orientation.

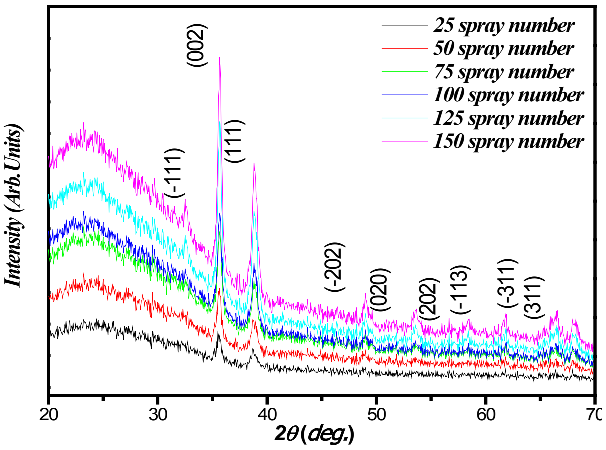

Fig. 1. XRD pattern of CuO thin films for different number of spray.

Figure 2shows the Raman spectra of CuO films for different spray number. The Raman spectra are composed of three main modes Ag and 2 Bg located at 277.27cm^{-1}, 333.11 cm^{-1} and 624.64 cm^{-1}. These peaks are widely reported in the literature [22-24]. This confirms the presence of a single CuO phase with a monoclinic structure as deduced from the diffraction analysis.Chaturvedi and Sathe[25] have studied the variation of Raman modes in CuO thin films by pulsed laser deposition as a function of thickness using Raman spectroscopy. They noted that the thickness increases leads to the increase in intensity of main Raman modes.

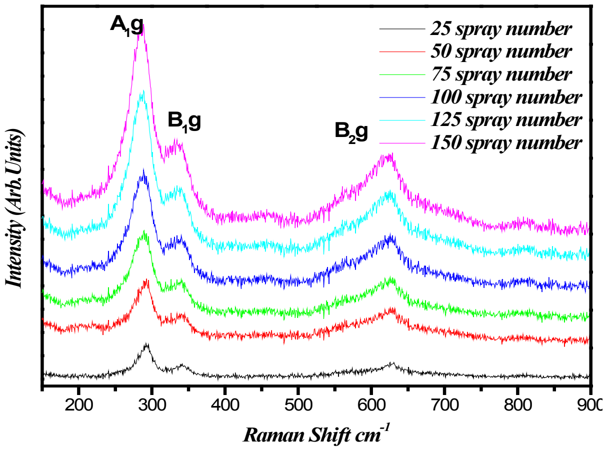

Fig. 2. Raman spectra of CuO thin films for different number of spray.

Copper oxide CuO has a monoclinic cell the size crystallite and internal strain of the oriented grains (002) is shown in Table 1.

Table 1. The peak position 2θ, FWHM, lattice parameter (a, b and c), crystallite size (D) and strain (ε) of the CuO thin films as a function of spray number.

Samples	2θ(deg.)	FWHM	a (Å)	b (Å)	c (Å)	D (nm)	ε (%)
CuO 25 spray number	34,414	0,330	4.52	5.31	3.421	32	0.58
CuO 50 spray number	34,431	0,302	4.58	5.24	3.422	37	0.48
CuO 75 spray number	34,436	0,301	4.62	5.21	3.423	45	0.41
CuO 100 spray number	34,425	0,252	4.67	5.12	3.423	50	0.35
CuO 125 spray number			4.53	5.19	3.423	62	0.28
CuO 150 spray number			4.46	5.23	3.423	68	0.22

According to the number of spray. The crystallite size D and the strain εinCuO thin films were calculated using the following relationships [26]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 sin^2\beta} - \frac{2hlcos\beta}{acsin^2\beta} \tag{1}$$

where$h$, k and l are the Miller indices. $d$is the lattice spacing calculated using the Bragg's equation and β= 99.45^0(took from the JCPDS card N^{0}45-0937).

$$D = \frac{0.9\,\lambda}{wcos\theta} \tag{2}$$

$$\varepsilon = \frac{w\cos\theta}{4} \tag{3}$$

where λ is the wavelength of the incident X-ray beam,$\theta$is the position of the diffraction peak considered and w is the mid-height width of the diffraction intensity (in radian).As can be seen in Table 1.

Table 1.shows the variation of the lattice parameters of CuO as a function of spray number; there is a concordance of the values with that reported in the literature [27-29].The lattice parameters a and c vary inversely. When the parameter a increases, as a function of the spray number, the parameter c decreases. May be due to the residual stress, which induced strain in the deposited films [22]. The lattice parameter b remains constant, as a function of the spray number.

The size of the crystalline D increases, depending on the number of sprays, from 32 to 68 nm. Crystal size values are comparable to those in the literature [30, 31]. The increase in crystalline size is due to the increase in the number of crystals (002) (considering that the intensity of the XDR peak is proportional to the number of crystals) which reflects an improvement in the crystalline structure of the deposited CuO films. Indeed, the increase in crystalline size reveals a decrease in the internal strain in the material.

The evolution of the thickness of the films of CuO as a function of spray number is shown in Figure 3. It is noted that the thickness of the films increases with the increase of the spray number, this correlation between the thickness of the films and spray number was also obtained by R.Daira and al and B.Boudjema and al [32, 33].

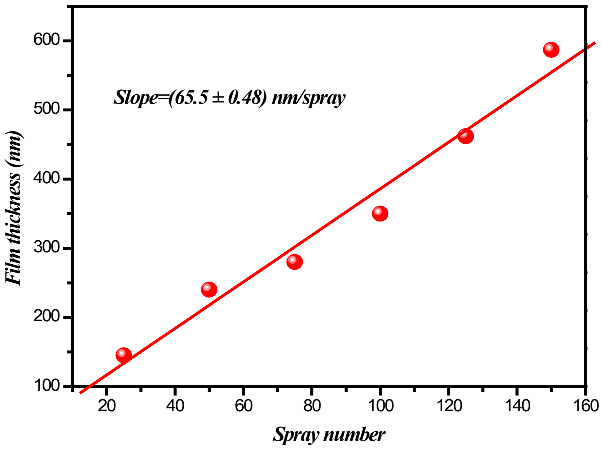

Fig. 3. Variation of film thickness of CuO as a function of spray number.

4.2.Optical characterization

Figure 4 Shows Optical transmittance spectra as a function of spray number, was studied within the wavelength range of 300 to 800 nm for all sprayed CuO thin films. The band optical energy in the case of a direct gap semiconductor such as CuO copper oxide can be given by the Tauc's law [34]:

$$(\alpha h\vartheta)^2 = A.(h\vartheta - Eg) \tag{4}$$

$$\alpha = \frac{\mathrm{Ln}(\frac{1}{T})}{e} \tag{5}$$

where Eg is the optical gap expressed in eV, T is the transmittance and e thickness of films a constant that characterizes the degree of disorder in an amorphous structure, α is the coefficient of absorption (dependent of the wavelength) and hν is the energy of a photon. These spectra are similar to those of CuO deposited using spray pyrolysis [35] and other methods [36, 37]. The films transmittance spectra are influenced by the spray. According to the (insert:Figure 4), one can observe that the transmission values decrease with an increase in the spray number. This result was caused by the increase in film thicknesses. For wavelength above 800 nm, the transmittance of the whole films is ranged from 40 to 80 %. This variation is in same range reported in the literature [38, 39]. CuO thin films are used as an absorber layers in solar cells. The high absorption of this layer in visible range is one of the required proprieties devices.

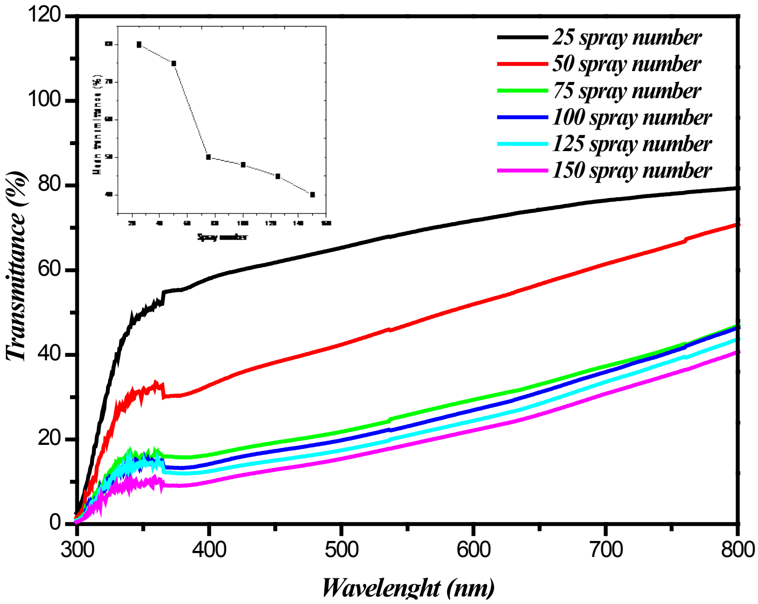

Fig. 4. Optical transmittance spectra as a function of spray number. (Inset: Variation of mean transmittance as a function of spray number).

The analysis of α in the visible region permit the energy gap calculation by linear fit of following relation: $(\alpha h\upsilon)^2 = f(h\upsilon)$. The intercept of the tangent to the plot will give a good approximation of the band gap energy for this direct band gap material.

The band gap energy corresponding to the CuO sprayed films elaborated with different spray number, ranges from 1.75 to 1.2 eV. This is shown in the Figure 5. One can deduce that the bandgap energy decreases with increasing the spray number.

The energy band gap decreases with increasing size of crystallite, and discrete energy levels appear in the band. When photons fall on a semiconductor, they will only be absorbed when the photon energy is sufficient to excite the electron. Of course, the band optical energy of CuO thin films is greater than the energy of the bulk material [40-42].

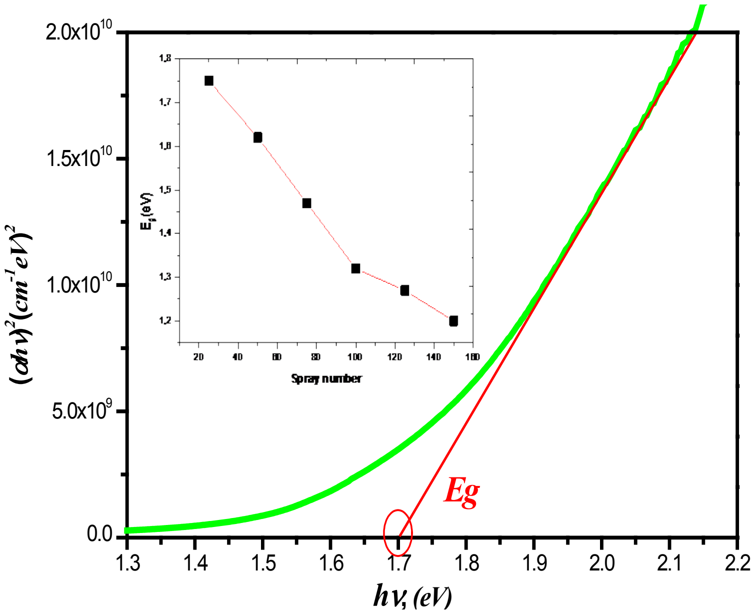

Fig. 5. Plot $(\alpha h\upsilon)^2$ as a function of photo energy. (Inset: Variation of band gap energy as a function of spray number).

4.3. Electrical characterization

The electrical properties in Figure 6. The thin films are of considerable interest in several applications such as solar cells, gas sensors. Among the electrical properties, resistivity is one of the important parameters. Resistivity is given by the following relation [34]:

$$\rho = \frac{\ln 2}{\pi} e(6)$$

where ρ is the resistivity and d is thickness of thin film.

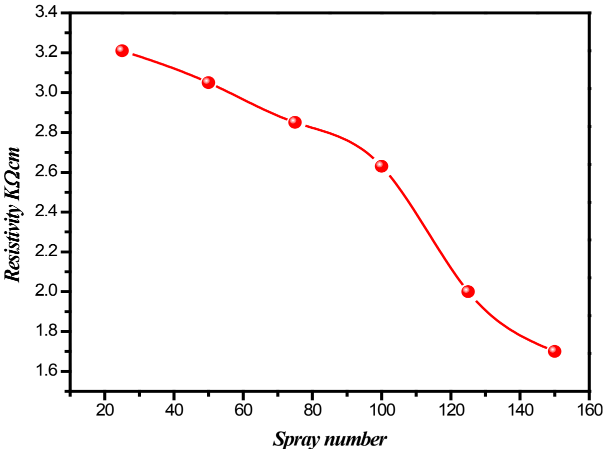

Fig. 6. Variation of resistivity of CuO as a function of spray number.

As shown in Figure 7. The resistivity values increase with the increasing of spray number. This is due to the increase of the grain boundaries, which corroborates with the obtained result in the XRD measurements (Figure 1).Through what C. Ravi Dhas et al have done to improve the morphological and structural properties of CuO films according to the different initial molar concentration prepared by spray pyrolysis, where it was intended to apply gas sensors, and compared to our results, it can be said that our prepared films, depending on the spray number of the solution, can be used in ethanol gas sensors application [43].

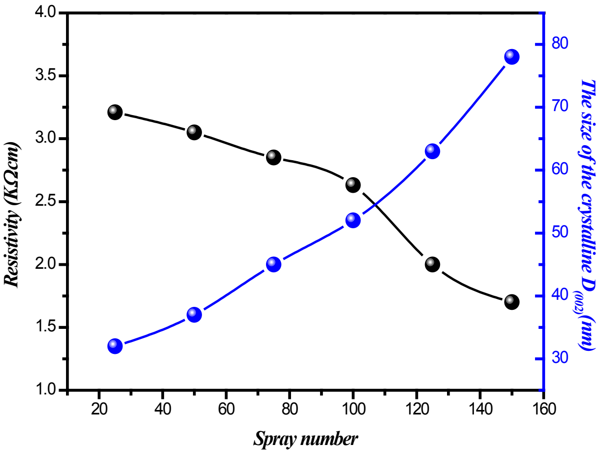

Fig. 7. Variation of size crystallite D and resistivity of CuO thin films as a function of spray number.

5. Conclusion

In this work, copper oxide (CuO) thin films were deposited using the discontinued spray pyrolysis method. The influence of spray number on films properties has been investigated their structural properties have been studied by X-ray diffraction (XRD) and Raman spectroscopy. According to the XRD, the deposited filmswere polycrystalline are mainly composed only with CuO mono phase along (002) plane. The Raman spectroscopy confirms the presence of a single phase CuO.The lattice parameters remains mainly constant, to study the optical and electrical characteristics we have, UV-Vis spectrophotometry and four-point method. We have found that our films are absorbent in the visible range where transparency starts in the NIR range, with an optical gap ranging from 1.75 to 1.2 eV, which is suitable for solar cells fabrication. In addition, the films have electrical resistivity in the range 3.21 KΩ.cm and 1.7 KΩ.cm. Finally, the ideal condition for better solar cell efficiency is increasing the spray number. From the results obtained, it can be said that it is suitable for ethanol gas sensors applications.

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