Structural, Electrical and Optical Properties of Fe-doped CuO Deposited by Spray Pyrolysis Technique

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ABSTRACT

Our work consists in depositing the copper oxide Fe doped CuO films by spray obtained from the solution of copper chloride CuCl2 and FeCl2 with a percentage of 2, 4; 6 and 8%, on glass substrates at a temperature of 3500c. The thin films obtained are characterized by X-ray diffraction, visible UV spectroscopy and the four-point technique.With X-ray diffraction, high peak intensity is obtained for the preferential orientations of (002) and (111), this intensity increases as the doping rate increases and gives us a more crystalline structure for a doping rate of 8%, also a grain size were estimated. The transmission of our films varies between 55% and 75% with a high absorption in the visible domain, the resistivity of our films increase with the increase of doping rate and the gap energy varies between 4.00 and 1.47 eV.

I. Introduction

Copper oxide CuO is a semiconductor material that is part of the transparent and conductive oxides (TCO), it has interesting electronic, electrical and optical properties for optoelectronic applications especially in the photovoltaic field. The band energy gap is of direct nature, the value of its optical gap is around 2.1 eV [1]. Copper oxides are used in several areas such as: gas sensors [2-6], solar cells [7-9] and light-emitting diodes [10]. The CuO films can be developed by several techniques such as: cathodic spray, laser ablation [11] and vacuum evaporation [12], chemical vapour deposition [12], sol-gel [13] and pyrolysis spray method [14, 15]. Our job is to obtain thin films of Fe doped CuO by spray spray. Our glass substrates are heated to a temperature of 3500C, the solution used in our work is copper chloride CuCl2 molarity of 0.1M as precursor and Fer chloride feCl2 molarity of 0.1 M as dopant.

The study of the physical properties of our films was carried out according to the growth of the grain size and optical gap being that the copper oxide is one of the TCO used (transparent and conductive oxides), the growth rate corresponding to optimal resistivity will be sought.

II. Experimental Procedure:

Fe-doped CuO copper oxide films were obtained from CuCl2 copper chloride and fer chloride with a molarity of 0.1 M, our 1*1 cm2 glass substrates were heated to a temperature of 3500 C, these films are deposited by continuous spray for different doping rates.

The crystalline structure was evaluated using a PhilipsX'Pert diffractometer with radiation (λ = 1.54 A0), which scans between 300 and 700. The optical transmission spectra were recorded with UV-Visible in the wavelength range 400-1000 nm. Electrical resistivity was measured with the four points.

III. Results and Discussion

III.1. Thickness Measurement

The thickness is measured using the surface profilometer, our calculated thickness is 762 nm.

III.2. Structural Properties XRD

The comparison of the data with the references of the JCPDS file (card N=° 45-0937) confirmed the cassiterite structure (monoclinic structure) of our films. The CuO phase was obtained around 2θ= 36.430, 38.510, 42.50, 47.330, 56.580, 60.770, and 64.130, which corresponds respectively to plans (002), (111), (-202), (020), (202), (-113), and (-311). (Figure 1).

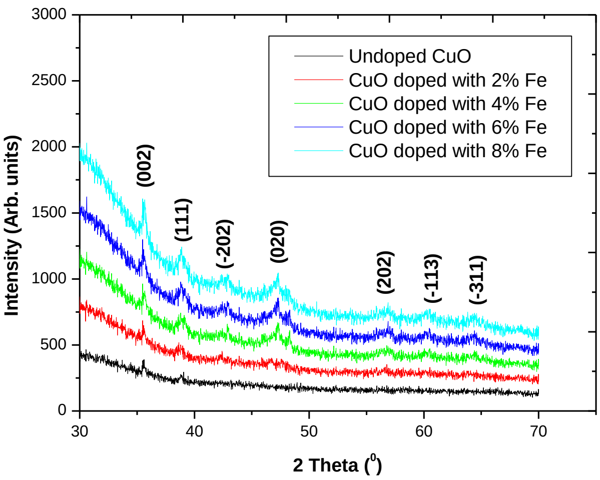

Figure 1. XRD patterns of Fe doped CuO thin films deposited using different doping rate.

The diffraction spectra show that our material has a poly crystalline structure. In all these films there are two preferential directions in the directions (002) and (111) the latter which is the most intense. The intensity of these two peaks increases with the increase in doping rate (Figure 2). A careful analysis of the diffraction patterns shows that there is no trace of iron related phase for all Fe-doped CuO compositions. This indicates that Fe ions were successfully doped into the lattice of Cu sites without affecting the crystal structure of the parent CuO matrix. The grain size of the most intense orientation (002) and the internal stress are calculated using the following formulas [16-17]:

$$D = \frac{0.9\lambda}{w.cos\theta} \qquad (1)$$

$$\varepsilon = \frac{w.cos\theta}{4} \qquad (2)$$

λ : is the wavelength of the incident X-ray beam.

w: is the width halfway up the diffraction line.

In Figure 3 we notice that average crystallite size decreases with increasing in Fe doping ratio indicating a small deterioration in the films'crystallinity.

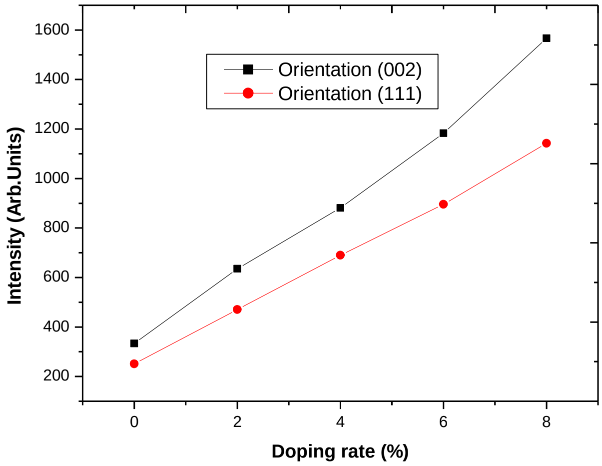

Figure 2. Variation of the (002) and (111) oriented crystallite size as a function of the doping rate.

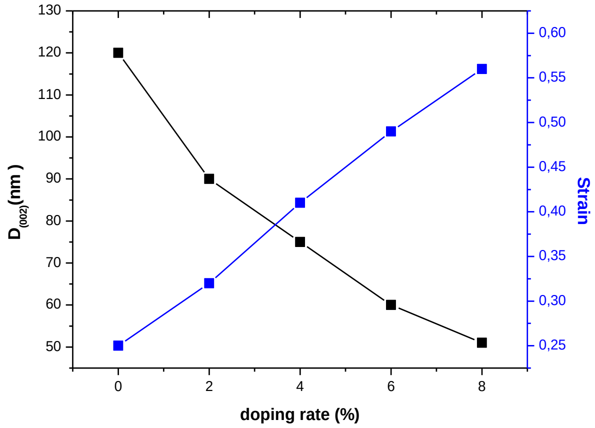

Figure 3. Variation crystallite size and the crystal strain as a function of the doping rate.

III.3. Optical properties

Figure 4 shows the optical spectrum transmittance of the Fe doped copper oxide films between 400 and 1000 nm.

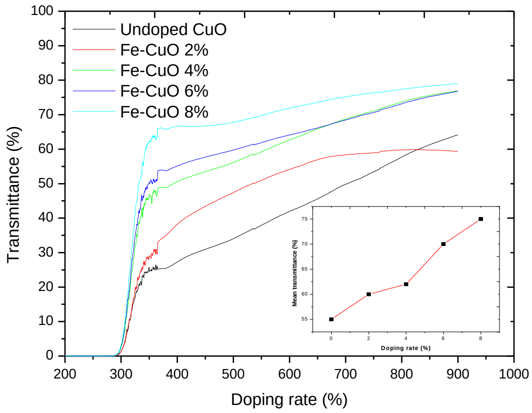

Figure 4. UV–visible transmittance spectra of the deposited Fe doped CuO thin films. (Inset: Variation of means

transmittance as a function of the doping rate).

In the spectra of our films, we distinguish two regions, a region of high transmission between 800 and 1000 nm, the transmission factor varies between 55% and 75%. And another region in the visible high absorption from which the absorption coefficient α is calculated from the formula of Beer Lambert [18-19]:

$$T = e^{-\alpha d} \rightarrow \alpha = -\frac{1}{d} lnT \qquad (3)$$

With: α is the coefficient of absorption and d the thickness of our films.

The gap energy will be calculated from the relationship [20-21]:

$$(\alpha h\vartheta)^2 = A * (h\vartheta - E_g) \qquad (4)$$

A: is a reflectant constant of degree of disorder of the amorphous solid structure, α: is the absorption coefficient (dependent on wavelength), and E is gap energy in eV. We represent the gap energy as a function of the doping rate (Figure 5). The results revealed that with increase in Fe doping amount, an increase in the transmittance was observed, it is around 75 % in the visible wavelength zone.

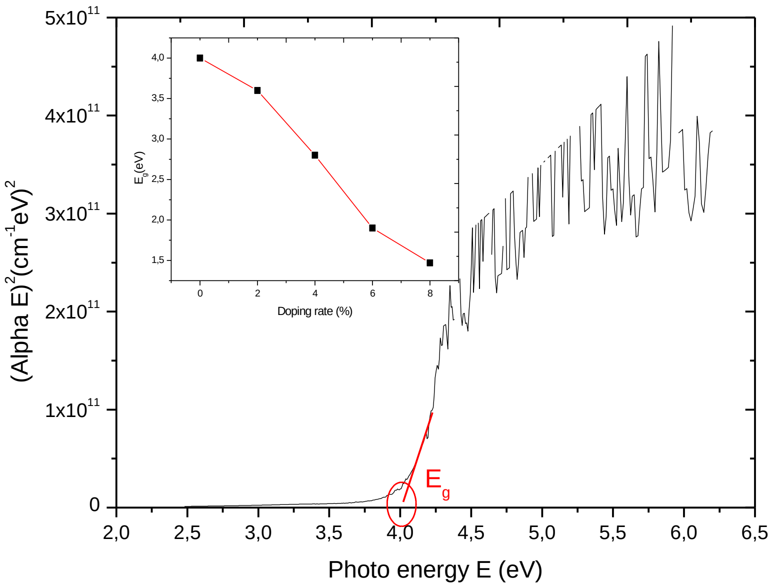

Figure 5. Plot of (αE)2 as a function of the photon energy E. (Inset: Variation of the band gap energy Eg as a function of the doping rate).

III.4. Electrical properties

The resistance of our obtained films is measured by the four points. The value of the resistivity ρ is related to the measurement of the ratio ΔV/I , according to the expression [22-26] :

$$\rho = \frac{\Delta V}{I} \frac{\pi\, d}{ln2} = R_s . d \qquad (5)$$

Where: d: film thickness of the material, Rs: surface resistance.

In Figure 6 we note that the resistivity of our films increases with the increase of the doping rate, this evaluation could be attributed to the increase of grain boundaries (Figure 6).

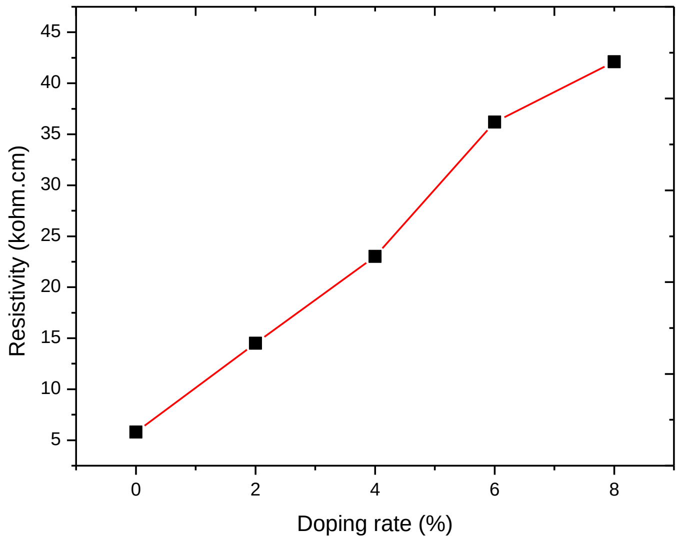

Fig 6. Resistivity of the deposited films Fe doped CuO.

IV. Conclusion

In this work, the Fe doped CuO thin films deposited with copper chloride were synthesized using a spray pyrolysis technique. We studied the influence of doping rate of Fe on the physical properties of our films, XRD results revealed that the prepared films had a polycrystalline nature. The incorporation of Fe did not change the monoclinic structure of CuO. The optical transmittance for the samples was below 75 %. The absorption band decrease with increasing in doping rate. The resistivity measurements show that the resistivity increases with increasing Fe concentration.

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