INVESTIGATION OF THE TEMPERATURE ON THE THIN LAYERS OF COBALT OXIDE PRODUCED BY THE SPRAY PYROLYSIS METHOD USING A SOLAR OVEN

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Article Info	Abstract
<p><i>Received: 10.09.2021</i> <i>Accepted: 23.11.2021</i></p> <p>Keywords: Co3O4, x-rays, optical gap, spray, solar</p>	<p>Thin films of cobalt oxide (Co3O4) were prepared on glass substrates by the spray pyrolysis method using a solar concentrator (oven) manufactured in our laboratory. We used different processing temperatures (300° C, 350° C and 400° C). The structural, optical and electrical properties of the different samples were analyzed by X-ray diffraction (XRD), UV-Visible spectroscopy and the Hall effect measurement system. X-ray diffraction observations revealed that cubic crystals are created in all films produced, and the film structure is that of a single phase created with preferential orientation along the (311) axis in films at low temperatures, and the axis (111) for high temperatures. The grain sizes of our products vary between (22.62nm and 66.19nm), depending on the processing temperature. The optical band gap of the crystals obtained was measured. The results of the optical forbidden bands of the crystals obtained, indicated two bands of the values for each element (Eg1 and Eg2). We observed that the values of the effective optical forbidden bands increase by 2.547eV and 3.0731eV with the increase in the production temperature., In addition the film produced experiences a decrease in the Urbach parameters which vary between 162.20meV and 360.81meV depending on the increase in production temperatures. Finally, the films produced have electrical conductivity values of (1.090 [(Ω.cm)⁻¹] to 1.853 [(Ω.cm)⁻¹] and electrical resistivity values of 1.431 (Ω.cm) at 1.853 (Ω.cm), depending on the variation in the production temperature.</p>

1. Introduction

Cobalt oxide (Co3O4) is an ionic chemical compound, made by decomposing cobalt chloride hexahydrate. The species likely to form during the oxidation of Co(OH)2 in a neutral and basic medium leads to the formation of Co3O4, Co2O3 or in hydrated form: Co(OH)3 or CoO2 [1]. Cobalt oxide Co2O3 is very metastable, its existence in the solid state has not yet been clearly verified [2]. Oxidation of Co(OH)2 in air results in the formation of Co2O3 and

the reaction proceeds rapidly until Co_3O_4 is obtained [3, 4]. It crystallizes, at temperatures below 450°C , in the cubic spinel structure in the same way as Fe_3O_4 [5]. It has a face-centered cubic structure, the mesh parameter is $8.080\text{\AA}$ and the space group $\text{Fd}\bar{3}\text{m}$ (type Al_2MgO_4). Despite the simple stoichiometry of Co_3O_4 , this spinel structure is much more complicated than CoO . Unlike CoO , this Co_3O_4 structure has two kinds of ions: Co^{+2} (II) in tetrahedral form and Co^{+3} (III) [3]. Is an important p-type semiconductor with direct optical bandgaps at 1.48 and 2.19 eV, and resistance to chemical and physical impacts [6]. However, the performance of thin films in general, and that of Co_3O_4 in particular, is most often dictated by the need for an increasingly high refractive index, an absorption coefficient as low as possible and a more polished surface. However, all this was only feasible with the technological advances recorded in the field of thin film deposition by the use of several physical deposition techniques such as reactive sputtering [7], evaporation by beam of electrons [8] and arc deposition [9, 10]. Also, it has become imperative to master the production processes of such materials, as well as the influence of the various parameters that imprint its properties on the finished material. Indeed, the limits of use of a given material are often the limits of its properties. Among these deposition techniques, the spray pyrolysis process appeared to us to be one of the simplest and most efficient thin film production methods in view of the (crystalline) quality ratio of the layers obtained with regard to cost price. As part of this work, we were interested in the study of the influence of the production temperature on the physicochemical, optical and electrical properties of thin films of Co_3O_4 obtained by the spray pyrolysis technique. To this end, we have developed a series of samples, deposited on glass substrates heated to processing temperatures (300°C , 350°C and 400°C).

2. Experimental procedure

2.1. Preparation of cobalt oxide substrates

Co_3O_4 thin films were prepared from cobalt chloride hexahydrate $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. Finally, methanol is poured into the solution to obtain a transparent solution of pink color and slightly viscous. The glass substrates were heated to the necessary processing temperatures (300°C , 350°C and 400°C) on a solar oven (Figure 1). The solution produced is mechanically sprayed onto hot glass substrates. To achieve the desired thickness, the deposition time is varied between 3 and 4 min, this period is expressed in several time intervals in order to give the layer sufficient time to crystallize. By placing the glass substrate on the heating plate of the oven under the crystallization temperature, then turn on the air nebulizer, then spray the solution for four minutes, then stop for a while until the substrate returns to its temperature, and we repeat the

process again until we obtain the required thickness. During this elaboration the temperature and followed by a thermocouple with a temperature range between "0°C to 1300°C".

According to the work presented by several authors, Bougrine, A., and al. [11], Chamberlin, R. and al. [12] Abbas, S. and al. [13], the spray pyrolysis method gives a more or less homogeneous product so that it cannot modify the properties from one zone to another. Especially since the spraying process is perpendicular to the substrate so that the solution is evenly distributed over the entire surface of the substrate. In addition to the temperature uniformity of the substrate on the hotplate.

Finally, after having developed the thin layers of Co₃O₄ (Figure 2), their structural, optical and electrical microstructural characterization is then carried out.

2.2. Characterization

X-ray diffraction (ARL TM EQUINOX 100 X-ray), UV-visible spectrophotometry (Cary Series uv-vis-NIR Spectrophotometer) and Hall effect measurement system (Ecopia HMS-3000) are the main analytical techniques. implemented in this study. By exploitation of DRX spectra, we can access the determination of the average grain size in a thin layer. By assuming that the grains are spherical, the relation of Scherrer [14, 15], allows the determination of the mean diameter through the following expression:

$$D_{(nm)} = \frac{0.90\lambda}{\beta \cos \theta} \quad (1)$$

Hence, D – the mean grain diameter, λ – the wavelength of the incident radiation ($\lambda = 1.54056 \text{ \AA}$), β – the width at mid-height of the diffraction peak, θ – the diffraction angle. The thickness of the deposits is measured with a mechanical probe profilometer placed on an anti-vibration plate in an air-conditioned room. The measured thicknesses of our films (Co₃O₄) were between 187nm and 195nm. From the values of the extinction coefficient k of the thin film, obtained by ellipso-metric measurements, the absorption coefficient α can be calculated, using the following relationship:

$$\alpha = 4\pi k / \lambda \quad (2)$$

The determination of the optical gap E_g is based on the model proposed by Tauc [15, 16], where E_g is related to the absorption coefficient by:

$$(\alpha E)^{1/2} = A(h\nu - E_g) \quad (3)$$

A is a constant reflecting the degree of disorder of the amorphous solid structure, E_g is expressed in eV, $E = h\nu$ is the energy of the photon in eV.

Due to the double presence of distinct phases, and the fact that no alloy was formed as indicated by XRD analysis; it is difficult to speak of a single gap in such a material, that is why we introduce a definition of an effective bandgap $E_{g\text{eff}}$ expressed as [17]:

$$E_{g.\text{eff}} = (1 - x)E_{g1} + xE_{g2} \quad (4)$$

To calculate the resistivity of our samples we used the principle of the Hall effect. This principle is based on two forces: Lorentz magnetic force and Hall electrical force in a semiconductor carrying a current and subjected to a magnetic field, hence the basic physical principle on which the Hall effect is based is the Lorentz force [18]. We used the Ecopia HMS-3000 system which has a magnet producing a 0.55T field to which the sample is subjected during electrical measurements using a dedicated holder. The device, using a sample holder of four tips arranged in a square and connected to a generator to perform the electrical measurements, is a complete system for measuring resistivity, Hall coefficient, concentration of carriers and their mobility. For our rectangular-shaped samples, the technique consists in taking four-point contacts A, B, C and D which alternately make it possible to inject a current I_h (in mA) between two contacts and to measure a voltage U_m (in V) between them. two others. By placing the contacts symmetrically (perfect square) and by taking the average of the different voltages U_m measured, we can deduce an average resistance R_m (in Ω) which will make it possible to determine the resistivity ρ ($\Omega\cdot\text{cm}$) of the thin film analyzed of thickness e (in cm) by the following relation:

$$\rho = \frac{\pi \cdot e R_m}{\ln(2)} \quad (5)$$

In order to determine the number of free carriers n (or p) (in cm^{-3}), it is necessary to measure the Hall voltage U_h taken between two contacts as soon as a current I_H is applied between the other two under the action a magnetic field B of 0.55 Tesla perpendicular to the sample. By permuting the orientation of this magnetic field, and by averaging the different measurements for each of these permutations, we can obtain the value of the average Hall voltage U_{hm} (in V) and determine n (or p) as well as the nature of the free carriers (electrons or holes) via the sign associated with the charge q (in C) thanks to the following formula:

$$n(\text{ou } p) = \frac{I_H \cdot B}{\pm q \cdot U_{hm} \cdot e} \quad (6)$$

Finally, knowing n and ρ , we can deduce the electronic mobility μ (in $\text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$) by the intermediary of relation (6):

$$\mu = \frac{1}{| \pm q . n . p |} \quad (7)$$

Figure 1. Experimental setup used

Figure 2. Substrate Co_3O_4

3. Results and Discussions

3.1 X-Ray Diffraction

Figure 3 shows that, all the films show diffraction peaks at $2\theta = 18.86^\circ$ and 36.59° respectively, correspond to the planes ((111) and (311) respectively), indicating the formation of crystals of a only Co_3O_4 material in the cubic structure, and all diffraction peaks in this model agree well with the standard map (JCPDS map No. 96-153-8532). We also noticed that in the low temperatures of the substrate, the plane (311) as preferential orientation, is a dominant plane

(especially in the case of temperatures 300°C and 350°C, on the other hand the plane (111) is the dominant plane in higher substrate temperatures (400°C). These results are consistent with the results of several authors who have worked on Co₃O₄, K. Klepper and al. [19] Y. Jiang and al. [20]. Zhan and al. [21], Abbas, S and al. [13], R. Manogowri and al. [22], A. Louardi and al. [23]. In this case, the surface energy of the (111) plane was lowest. When the temperature of the substrate increases, and the grains of the thin films will then have a very strong tendency to orient themselves coherently during the preparation of the sample towards this plane. The average size of the crystallites D at peak (111) increases by 34.64nm at 49.19 nm with increasing substrate temperature up to 350°C, then decreases to 34.65nm at temperature 400°C. This can be attributed to the fact that a high temperature of the substrate increases the formation of polycrystalline film with a better crystalline [23, 24]. The values of the preferential orientation TC (hkl), of the planes (111) and (311) increase continuously with the increase in the production temperature, but the values of the plane (311) experience a decrease after 350°C (Table 1). In addition, we have found the plane (311) as the preferential orientation for the entire temperature range and (111) exhibits a preferential orientation than in higher substrate temperatures (350°C to 400°C). This phenomenon can be attributed to the increase in the density of oxygen and the decrease in the density of cobalt in thin films. Several authors, M. Manickam and al. [25], Abbas, S. and al. [13], N. Kouidri and al. [26], have found the same results. The dislocation density δ and the deformation ϵ of Co₃O₄ films are reduced with increasing temperature up to 350°C, after this temperature, the values of δ and ϵ increase with increasing temperature (Table 1). This observation is the same for the plans (111) and for the plans (311). We observe an inverse relationship with the size of the crystallites.

Table 1. The acoustic parameters of Co₃O₄ (T)

	hkl	2 θ [°]	d[Å]	D[nm]	a[Å]	$\delta \cdot 10^{14}$ [line/m ²]	$\epsilon \cdot 10^{-3}$	Tc(hkl)
T=300°C	(111)	18.75	4.7	34.64	8.15	8.33	11.62	0.095
	(311)	36.42	2.45	27.61	8.14	13.11	15.15	0.013
T=350°C	(111)	18.86	4.67	49.19	8.09	4.13	8.19	0.098
	(311)	36.49	2.45	27.35	8.14	13.37	15.3	1.61
T=400°C	(111)	18.87	4.68	34.65	8.1	8.33	11.62	0.105
	(311)	36.27	2.48	27.21	8.21	13.51	15.36	0.014

Figure 3. Acoustic parameters of Co₃O₄ thin films as a function of temperature

Figure 4 shows typical absorbance spectra recorded for thin films of Co₃O₄ at different processing temperatures. In this figure, we can notice that the thin films deposited are completely transparent in the visible and start to absorb in the range between 300 and 350 nm, that is to say in the near ultraviolet. With the increase in temperature, there is a shift in the absorption threshold towards longer lengths indicating the increase in the gap of the Co₃O₄ films.

Figure 4. Absorbance spectra of Co₃O₄ thin films as a function of processing temperatures

3.2. Optical properties

Figure 5 represents the evolution of the optical gaps of thin films in Co₃O₄. The values of two direct forbidden bands were named Eg1 (lower energy region) and Eg2 (higher energy region). The multiple optical gap energies for Co₃O₄ films may suggest the possibility of valance tape degeneration [27]. The values of the effective optical gaps vary between (1,923eV and 2,074eV). It is clear to observe that all the values of the optical gaps are increased with the evolution of the temperature. As we have seen in Table 2, the values of Eg1 and Eg2 pass respectively from 1.720eV to 1.816eV and from 2.547eV to 3.073 eV, and these values are in good agreement with the results of other authors who work on the same axis Abbas, S and al. [13], [25, 28]. This change could be attributed to changes in the quality of Co₃O₄ films with increasing substrate temperature [23]. The energy of the forbidden bands increases the temperature of the substrate, when the oxygen atoms are increased, the holes fill the states in the valence band, which leads to the shift of the Fermi level towards the low energies. The band gap measured from the inter-band absorption changes to a higher energy (blue shift) [26]. Figure 6 represents the evolution of the values of the Urbach energies as a function of the production temperature, it is clear to note that the values of the Urbach energies decrease with the increase in temperature (change inversely with the optical band gap). This means that when the temperature of the substrate increases, the influence of the tails of the bands on the energy of the band gap becomes weaker [29].

Table 2. Optical results of the thin films produced.

	Eg1[eV]	Eg2[eV]	Egef[eV]	Eu1[meV]	Eu2[meV]
T=300°C	1.932	1.720	2.547	245.01	360.81
T=350°C	2.004	1.781	2.680	180.29	352.94
T=400°C	2.074	1.816	3.073	162.20	330.32

Figure 5. Optical gaps of Co3O4 thin films

Figure 6. The Urbach parameters (E_u) of Co3O4 thin films

3.3. Electrical properties

In order to verify the quality of our contacts, the $I - V$ measurements (Figure 7) were carried out at room temperature between the contacts (ab, bc, cd and da) on the surfaces of Co3O films having different thicknesses (360, 332 and 381 nm). The trace $I - V$ at the level of the terminals (ab, bc, cd and da) presents in each of the configurations a linear form. This fact means that the contacts are of the ohmic type, thus making it possible to measure the

transport properties of our samples.

Table 3. Electrical results of Co₃O₄ as a function of temperature.

	$n[\text{cm}^{-3}]$	$\mu[\text{cm}^2/\text{V.s}]$	$\sigma[(\Omega.\text{cm})^{-1}]$	$\rho[(\Omega.\text{cm})]$	$e[\text{nm}]$
300°C	6.935E+18	3.967E+02	1.853	1.431	360
350°C	2.355E+18	1.430	1.090	1.853	332
400°C	2.355E+18	6.292E-01	1.431	1.853	381

Table 3 groups together the data deduced for Hall mobility μ , the concentration of free electrons n and the resistivity ρ measured at ambient temperature. The study shows that the conduction is p-type for all Co₃O₄ thin films. The measurements show on the one hand, the more the production temperature increases, the more mobility decreases and that, on the other hand, Co₃O₄ films are relatively conductive (10 $\Omega.\text{cm}$).

Figure 7. Curves $I = f(V)$ of the contacts (terminals ab, bc, cd and da) of Co₃O₄ thin films

This consequently leads to a reduction in the lifetime of the carriers which then

generates a decrease in the mobility and the concentration of the carriers, ultimately leading to a low conductivity of the films, which is high enough to constitute a good electrode material. super capacitor. This is because stoichiometric Co_3O_4 is an insulator and its electrical properties depend on the amount of oxygen adsorbed on the surface. A similar behavior of electrical conductivity has been reported by Patil et al. and Gencyılmaz and al. [25, 30].

4. Conclusion

A solar concentrator used as an oven has been successfully produced. Thanks to this device, the pyrolysis spray method was applied. The oxides used (cobalt oxide) are sprayed by a nebulizer and its airbrush, under the effect of pressure which transforms the starting solution into a jet of very fine droplets. The good optical characterization of the glasses which adapts well for their transparency to thin films, and their resistance to heating up to 600°C , led us to choose rectangular glass slides of $1.5\text{cm} \times 5\text{cm}$, and thickness equal to 1mm . Very good quality thin films of cobalt oxide (Co_3O_4) are produced at various temperatures (300°C , 350°C and 400°C). The thin films produced are nanocrystalline with a face-centered cubic CFC structure. Where the (311) plane is a dominant plane in all cobalt thin films except films produced at high temperatures, where the dominant plane is (111). All the deposits in planes (311) and (404) are polycrystalline with values of the preferential orientation varying between (0.014 and 1.61). The maximum value of the grain size reaches a value of 49.19 nm , for an elaboration temperature of 350°C . Our developed products have presented dislocation density values that vary between $8.33 \times 10^{14} [\text{line} / \text{m}^2]$ and $13.51 \times 10^{14} [\text{line}/\text{m}^2]$, and strain values ranging between $8.19 \times 10^{-3} [\%]$ and $15.36 \times 10^{-3} [\%]$. The effective optical gap values which vary between (2.547eV and 3.0731eV), with variation of the Urbach parameters between 162.20meV and 360.81meV . Finally our elaborated films are relatively insulating conductors, with values of electrical conductivities between ($1.090 [(\Omega.\text{cm})^{-1}]$ and $1.853 [(\Omega.\text{cm})^{-1}]$), and resistivities between ($1.431 [(\Omega.\text{cm})]$ and $1.853 [(\Omega.\text{cm})]$).

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