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INFLUENCE OF THE CONDITIONS OF THE THERMAL TREATMENT ON THE ELECTRICAL PROPERTIES OF COBALT OXIDE LAYERS

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The influence of thermal treatment (different annealing atmospheres) on the electrical properties of cobalt oxide thin layers was studied. The layers were fabricated by sol-gel technique. Electrical properties were determined by the four–point probe method and Van der Pauw technique. The film resistivity decreases with temperature which confirms the semiconductor nature of the film. For the same film thickness value, the layers exposed in air exhibit conductivity values of order $10^{-3}\Omega^{-1}cm^{-1}$, while for the layers treated in forming gas (H_2/N_2) the conductivity is 10^6 times greater. The activation energy decreases with increase in film thickness.

INTRODUCTION

Cobalt oxide is used as semiconductor and electrochromic material,[1] in pigments for ceramics and glass, in fast drying paints and varnishes, in enamel coatings on steel, etc.

Cobalt forms two stable oxides: CoO and Co_3O_4, both of them having a cubic lattice. Co_3O_4 has a normal spinel structure, where Co^{2+} ions occupy the tetrahedral sites while the Co^{3+} the octahedral sites. Both oxides are normally non-stoichiometric, with an excess of oxygen. This excess yields a p-type semiconducting behavior.[2]

Thin films of cobalt oxide have been prepared from various deposition techniques: spray pyrolysis, sputtering, chemical vapor deposition, sol–gel process technique, electrophoresis, etc., on a variety of substrates. [3-6]

This paper reports the influence of thermal treatment on the electrical properties of cobalt oxide thin films prepared by using a sol-gel method.

EXPERIMENTAL

In this work we have analyzed two groups of films. Each group contains films with different thicknesses (different number of layers). Both groups were prepared by dip coating technique, by immersing the support (Corning Glass) in the same colloidal solution, using the same withdrawal speed and having different number of layers. One layer is obtained after one dipping-drying-calcination cycle. The resulted films were subjected to different thermal treatments. One group of films was heat at 500ºC, 2h in air and the other one at 500ºC, 2h in forming gas (H_2/N_2).

The film thickness was measured by using a Linnik interferential microscope.

Structural analyses of cobalt oxide films were performed by X-ray diffraction with a Rigaku diffractometer and an atomic force microscope (AFM) was employed to analyze the surface morphology of the films. The electrical parameters measurement was made using the four–point probe method and the Van der Pauw technique.

Van der Pauw technique[7,8] is a combination of a resistivity measurement and a Hall measurement. This technique uses a thin-plate sample containing four very small ohmic contacts placed on the periphery of the plate. A schematic of a rectangular van der Pauw configuration is shown in Fig. 1.

Van der Pauw demonstrated[8] that there are two characteristic resistances R_A and R_B, associated with the corresponding terminals shown in Fig. 1. To obtain the two characteristic resistances, one applies a DC current I into contact 1 and out of contact 2 and measures the voltage V_{43} from contact 4 to contact 3 as shown in Fig. 1. Next, one applies the current I into contact 1 and out of contact 4 while measuring the voltage V_{23} from contact 2 to contact 3. R_A and R_B are calculated by means of the following expressions:

$$R_A = \frac{V_{43}}{I_{12}} \quad ; \quad R_B = \frac{V_{23}}{I_{14}} \tag{1}$$

R_A and R_B are related to the sheet resistance R_S through the van der Pauw equation:

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$$\exp\left(-\frac{\pi R_A}{R_S}\right)+\exp\left(-\frac{\pi R_B}{R_S}\right)=1 \qquad (2)$$

The bulk electrical resistivity ρ_V can be calculated using $\rho_V = R_S \cdot t$, where t is the thickness of the film.

The same sample can also be used for the Hall measurement(Fig.2). To measure the Hall voltage U_H, a current I is forced through the opposing pair of contacts 1 and 3 and the Hall voltage U_H (= V_{24}) is measured across the remaining pair of contacts 2 and 4. Once the Hall voltage is acquired, the sheet carrier density n and the mobility μ can be calculated.

The four point probe(Fig.3) contains four thin collinearly placed tungsten wires probes which are made to contact the sample under test. Current I is made to flow between the outer probes, and voltage V is measured between the two inner probes, ideally without drawing any current.

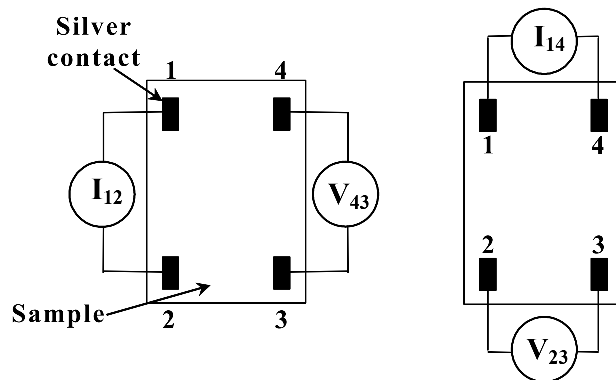

Fig. 1 – Scheme of the Van der Pauw technique.

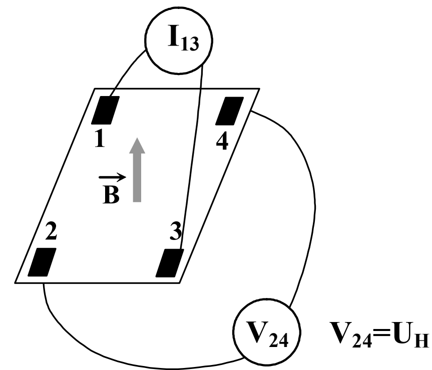

Fig. 2 – Scheme of Hall voltage measurement.

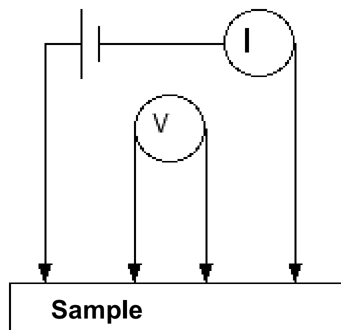

Fig. 3 – Four–point probe method scheme.

If the sample is of semi-infinite volume and if the interprobe spacings are $s_1 = s_2 = s_3 = s$, then it can be shown that the resistivity of the semi-infinite volume is given by

$$\rho_\infty = 2\pi \cdot s \cdot \frac{U}{I} \qquad (3)$$

Practical samples are of finite size. For the cases when the sample thickness is ≤ 5s, the resistivity become:

$$\rho = a \cdot 2\pi \cdot s \cdot \frac{U}{I} = a \cdot \rho_\infty \qquad (4)$$

where a is the correction factor. In our case, the ratio $\frac{t}{s} \le 0,5$

so $a = 0,72 \cdot \frac{t}{s}$. When substituted into the basic equation we get:

$$\rho = a \cdot 2\pi \cdot s \cdot \frac{U}{I} \to \rho = 4.532 \cdot t \cdot \frac{U}{I} \quad (\Omega \cdot cm) \qquad (5)$$

The sheet resistance , R_S is:

$$R_S = \frac{\rho}{t} = 4.532 \cdot \frac{U}{I} \quad (\Omega) \qquad (6)$$

RESULTS AND DISCUSSION

Fig. 4 shows the diffraction spectrum of two cobalt oxide thin films prepared using the same parameters (concentration of the colloidal solution, withdrawal speed, number of layers).

In the spectra of the film exposed 2h in air (a), there is a highest intensity peak at 2θ=36.7° which is accounted for a reflection of the X radiation onto the (311) planes[5]. This peak together with other small ones indicates the existence of Co_3O_4 as disperse phase. The (b) XRD pattern revealed that in the film annealed in reducing atmosphere (H_2/N_2) a reduction of Co^{3+} to Co^{2+} occurs.

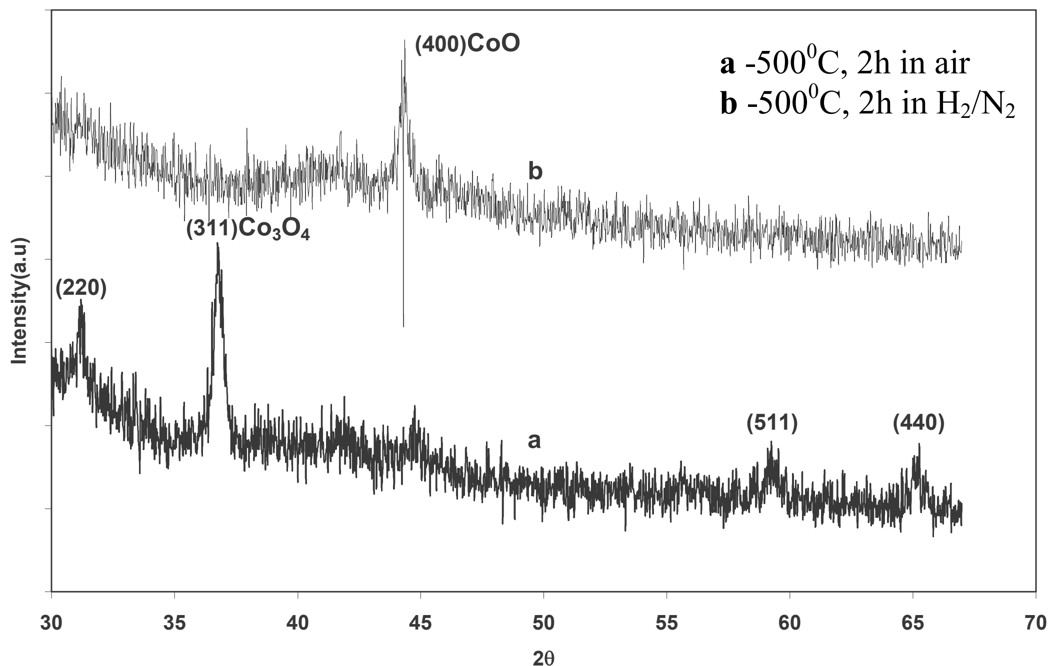

Fig. 4 – XRD patterns of cobalt oxide films annealed at 500ºC: a) 2h in air; b) 2h in H_2/N_2.

When the films are exposed in H_2/N_2, they consist of CoO phase and the crystallites have a preference growth to the (200) orientation [6].

According to AFM measurements (Fig. 5), the two groups of films are homogeneous and crack-free.

The grains are uniform in size and shape. The mean crystallite size, D_m, which was found from the AFM, grows when the film is exposed in H_2/N_2. The film presented in the pictures below has a mean crystallite size of 12.8 nm when is treated in air and 23.77 nm when is exposed in H_2/N_2.

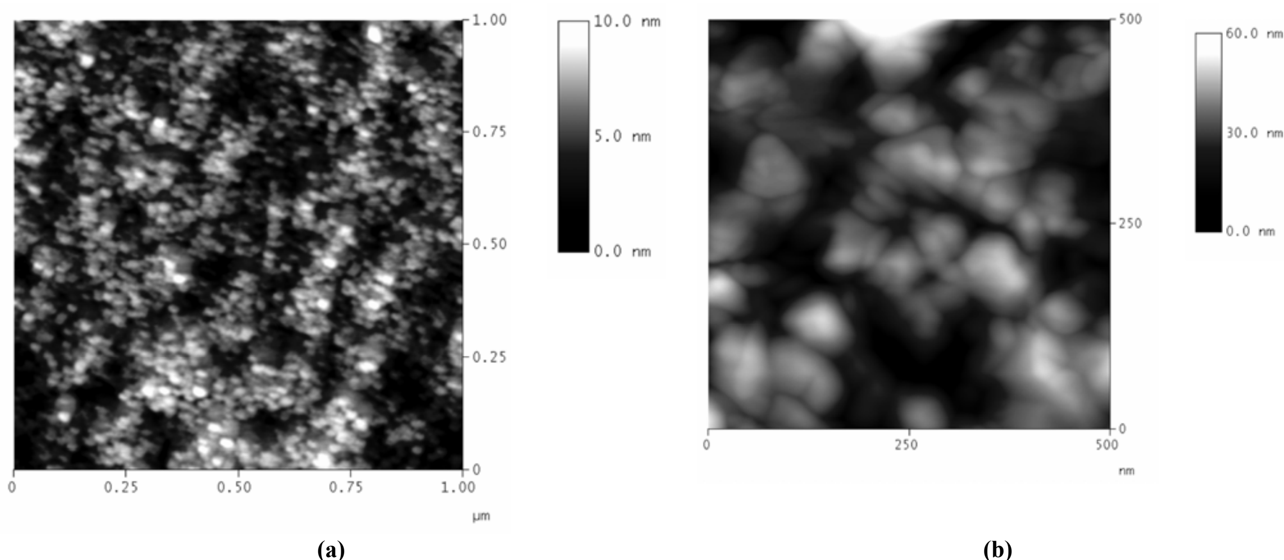

Fig. 5 – AFM pictures of cobalt oxide films annealed at 500ºC: a) 2h in air; b) 2h in H_2/N_2.

The values of room temperature resistivity, ρ, measured using the four–point probe method, were of order 10^2 Ω·cm for the group of films treated in air. For the films exposed in H_2/N_2, the values are in the range of 10^{-4}Ω·cm. In both situations, the room temperature resistivity decreases with increasing film thickness. About the same values we have obtained by using the Van der Pauw technique based on the Hall effect (Table 1).

By measuring the Hall voltage, we could find the type of carriers, the carrier density (p) and

mobility (μ), Hall coefficient and the sheet resistivity (ρ), and also the electrical conductivity of the films, as presented in table 1.

Table 1

Electrical parameters of cobalt oxide films with different thicknesses (t) and submitted to different thermal treatments

	t (nm)	ρ for 300K (Ωcm)	p (cm^{-3})	μ (cm^2/Vs)	σ for 300K ($\Omega^{-1}cm^{-1}$)
Films treated in air 500°C	166.1	227.595	$4.62\cdot10^{15}$	20	$4.39\cdot10^{-3}$
	177.2	194.5672	$5.08\cdot10^{15}$	17	$5.14\cdot10^{-3}$
	218.1	93.99	$8.54\cdot10^{15}$	8.26	$10.6\cdot10^{-3}$
	225.9	62.1784	$12.5\cdot10^{15}$	5.46	$16.1\cdot10^{-3}$
Films treated in H_2/N_2 500°C	100.6	$2.16\cdot10^{-4}$	$1.27\cdot10^{22}$	11.2	$4.62\cdot10^{3}$
	109.98	$1.49\cdot10^{-4}$	$1.72\cdot10^{22}$	7.54	$6.71\cdot10^{3}$
	118.78	$1.14\cdot10^{-4}$	$2.10\cdot10^{22}$	5.77	$8.81\cdot10^{3}$
	122.87	$4.44\cdot10^{-5}$	$3.91\cdot10^{22}$	2.25	$2.25\cdot10^{4}$

The conduction in both cases was attributed to holes. For the same value (t) of the film thickness, the layers exposed in air exhibit conductivity values (σ) of order 10^{-3} $\Omega^{-1}cm^{-1}$, while for the layers treated in forming gas (H_2/N_2) the conductivity is 10^6 times greater.

As we could see in our previous work [9], in thicker films appears an improvement in crystallinity and grain size which induce higher conductivity.

The carrier density increases with increasing thickness and it is 10^6 times greater for the films exposed in H_2/N_2.

Because the diffusion coefficient of hydrogen is higher, we assume that it get easily into the crystals inner space generating dislocations. The impurities and the defects increase the carrier density and implicitly the conductivity of extrinsic semiconductors[10].

Using the same technique, the variation of the electrical resistivity with temperature (Fig. 6) was studied. The resistivity of the film decreases with temperature, which confirms the semiconductor nature of the film. The films are p-type semiconductors.

The activation energy (E_a) was calculated from the plot lnρ = f(1/T) (Fig.6) according to formula:

$$\ln\rho = \ln\rho_o + \frac{E_a}{kT}$$

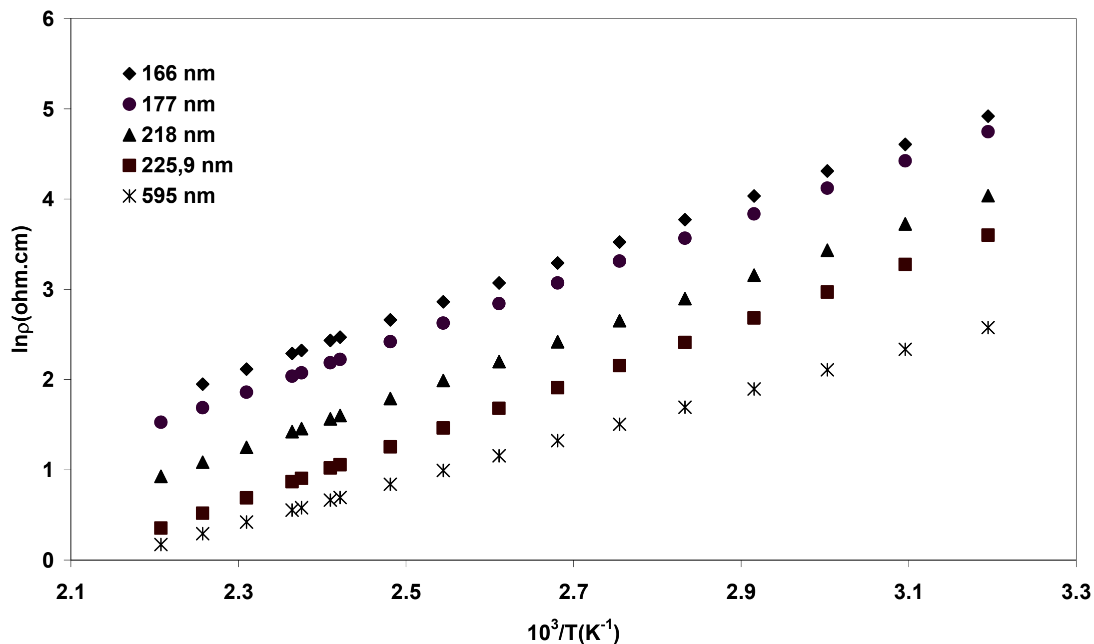

Fig. 6 – Variation of ln ρ versus 1/T for cobalt oxide films of various thicknesses.

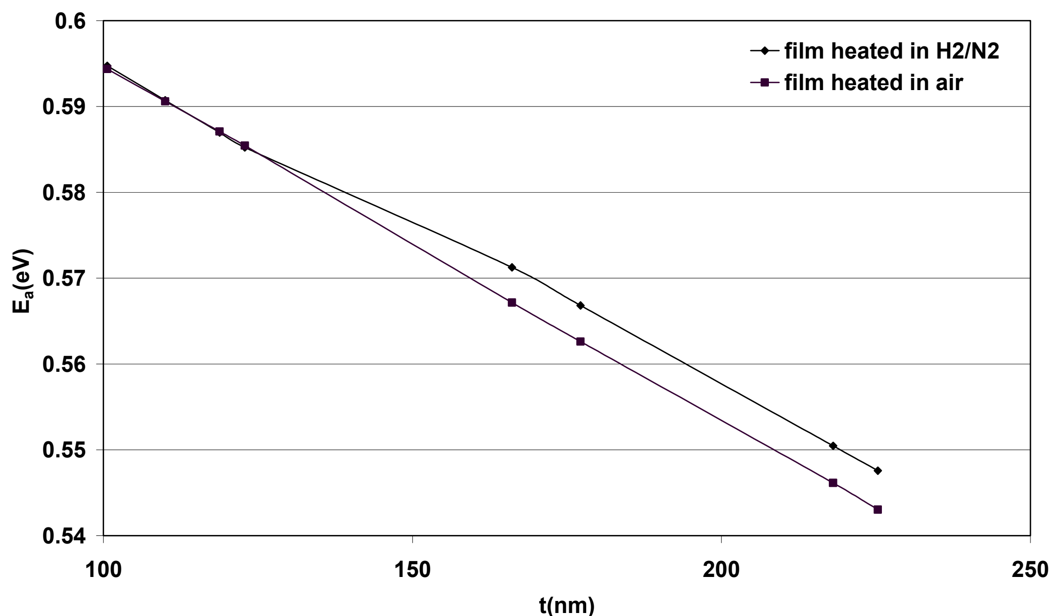

Fig. 7 – Variation of activation energy with film thickness.

The activation energy decreases also with increasing thickness from 0.567 eV at 166 nm to 0.42 eV for 595.378 nm.

The energy values have about the same values for the films exposed in H_2/N_2 and for those in air exposure (Fig. 7).

CONCLUSIONS

In this paper we studied the influence of thermal treatment on the electrical properties of cobalt oxide thin layers. The layers were fabricated by the sol-gel method, through the dip coating technique. The analyzed films were prepared by using the same deposition parameters.

The films are p-type semiconductors and their conductivity increases for thicker films.

For the same thickness, the films treated in forming gas exhibit conductivity values 10^6 times greater than the films exposed in air. The activation energy decreases with increasing film thickness and this decrease was found to be non-linear.

REFERENCES

1. P.S.Patil, L.D.Kadam and C.D.Lokhande, *Thin Solid Films*, **1996**, *272*, 29-32.
2. L.Pauling, “Chimie Generală”, Editura Ştiinţifică, 1972.
3. P.Pejova, A.Isahi, M.Najdoski and I.Grozdanov, *Mater.Research Bull.*, **2001**, *36*, 161-170.
4. L.D.Kadam and P.S.Patil, *Mater.Chem.Phys.*, **2001**, *68*, 225-232.
5. L.M.Apátiga and V.M.Castaño, *Thin Solid Films,* **2006**, *496*, 576 – 579.
6. A.U.Mane and S.A. Shivashankar, *J. Cryst.Growth*, **2003**, *254*, 368-377.
7. http://www.eeel.nist.gov/812/intr.htm
8. J.van der Pauw, *Philips Techn.Rev.*, **1958**, *8*, 220.
9. R.Draşovean and N. Ţigău, 8th International Conference on Physics of Advanced Materials, June 4-7, Iaşi, Roumania, **2008,** 47.
10. C.Tudose, I. Cucurezeanu and N.Velican, “Fizică”, Editura Didactică şi Pedagogică, 1981.