



Correlation Studies between Sol Aging Time and Substrate Dipping Time Parameter and Optical Properties of Cobalt Oxide Layers

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Abstract

Cobalt oxide films represent an important class of materials which are characterized with good electrochemical, catalytic and optical properties [1]. Many articles proved that sol-gel deposited cobalt oxide thin films possess suitable optical properties as selective coatings. In this work, the optical properties of cobalt oxide thin films, prepared by sol-gel dipping technique, are analyzed as a function of the aging time of the sol and of the dipping time of the substrate into the sol. UV-VIS spectroscopy was used for this purpose. The optical constants for these films are reported as a function of the two studied parameters, for the 300-800 nm spectral range. The structural characterization of the films was made by means of the X-ray diffraction technique. We demonstrate that, by increasing the dipping time, the size of the Co₃O₄ crystallites increases. We also prove that sol aging leads to an increase of the optical band gap of these films. The thickness of the films was also found to dependent on the sol-aging and on the immersion time.

Keywords: cobalt oxide; dipping time layer; sol-ageing time; film; optical properties.

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1. Introduction

Nanostructured materials receive special attention due to their performance in electronics, optics and photonics. With the particle size reduction new electrical, mechanical, chemical and optical properties appear. These properties are due to surface effects and the quantum confinement.

Such a material with special properties and multiple applications is cobalt oxide. We studied two stable forms, namely Co_3O_4 and CoO .

Co_3O_4 has the spinel structure with cobalt(II) in tetrahedral sites and cobalt(III) in octahedral sites. It is a black antiferromagnetic solid. CoO has a rock salt structure and is antiferromagnetic below 16°C [2].

Spinel-type cobalt oxide (Co_3O_4) is a material with applications in lithium ion batteries, heterogeneous catalysts, gas sensing, ceramic pigments, and electrochemical devices [3]. Cobalt oxide films are protective against localized corrosion and present various applications such as solar thermal energy collectors [4], ion-storages [5], chemical sensors [6] and electro chromic (EC) devices [3].

In this paper, we report the study of the dependence of the structure and optical properties of cobalt oxide films, deposited by sol-gel dipping as functions of the aging time of the sol and of the dipping time of the substrate in the sol. These are key-factors for the preparation of sol-gel-deposited films. Thus, they influence the crystallinity of the films and, inherently, they will determine the values of their optical parameters.

2. Materials and methods

As stated above, the sol-gel technique was employed for the preparation of cobalt oxide films. Glass substrates were immersed into a colloidal solution.

The colloidal solution was prepared by dissolving cobalt acetate, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in methanol. After dipping the substrates for several times, the samples were dried. Heating the samples up to 300°C , the dried gels were converted into solid state oxide films. The samples were, then, submitted to different thermal treatments, in order to improve their optical properties.

Two preparation parameters are chosen here for the study of their influence on the structure and on the optical characteristics of the cobalt oxide films. These parameters are: the aging time of the sol and the dipping time of the substrate in the sol.

The structural analysis of the films was performed by means of X-ray diffraction (XRD). A Rigaku diffractometer was used, operating with a $\text{Cu K}\alpha$ target, emitting the $\lambda=1.5418 \text{ \AA}$ line.

The size of cobalt oxide crystallites was determined with Scherer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where $\lambda=1.5418 \text{ \AA}$, β is the full-width-at-half-maximum of a certain XRD peak and θ is the Bragg angle.

The thickness of the films was measured with two methods: by using a surface profiler (Veeco, Dektak3) and by means of a Linnik MII-4 interferential microscope. The UV-visible transmittance spectra of the films were obtained with a Shimadzu spectrophotometer.

In order to determine the optical band gap values, the optical absorption data were analysed using the Tauc law [7]:

$$\alpha h\nu = A(h\nu - E_g)^p \quad (2)$$

where E_g is the optical band gap, A a constant and p is a number depending on the type of optical transition, being $1/2$ for direct allowed transitions and $3/2$ for forbidden transitions, respectively. Indirect optical transitions were proved and studied by using the following formula [8, 9]:

$$\alpha h\nu = B(h\nu - E'_g \pm E_p)^q \quad (3)$$

Where E'_g is the indirect energy bandgap, E_p denotes the photon energy and B is a constant. The q index equals 2 for indirect allowed transitions and changes to 3 for forbidden transitions, respectively.

3. Results

From the XRD patterns of the studied films, it was found that they are polycrystalline, consisting of the Co_3O_4 oxide. Figure 1 presents the XRD patterns of the Co_3O_4 films as a function of the dipping time of the substrate into the sol. Instead, figure 2 depicts the XRD spectra of the cobalt films as changing with the sol aging. Both sets of diffraction patterns from figures 1 and 2 exhibit one major peak at $2\theta=36.8^\circ$, which corresponds to the (311) plane, according to the JCPDS database [10,11]. Two other peaks, corresponding to the (220) and (440) planes can be noticed.

By studying the diffraction spectra presented in figure 1, it was noticed that the intensity of the XRD peaks slightly increases with increasing dipping time.

Table 1 presents key structural characteristics of the Co_3O_4 films, as a function of the dipping time. As expected, the thickness of the films increase with increasing dipping time, as more oxide material deposits for dipping the substrates into the sol for more times.

It can be also notice that, there is a slight increase of the diameter of the crystallites with increasing dipping time which, correlated with increasing intensity of the XRD peaks leads to the conclusion that the crystallinity of the

films improves with increasing dipping time of the films substrates.

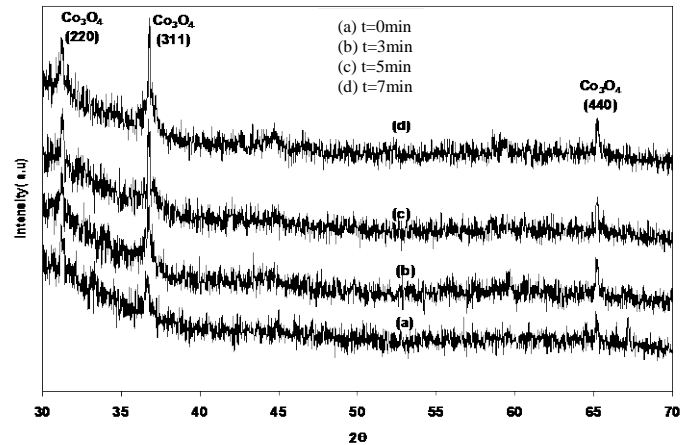


Figure 1:The XRD spectra of Co_3O_4 films with different dipping time

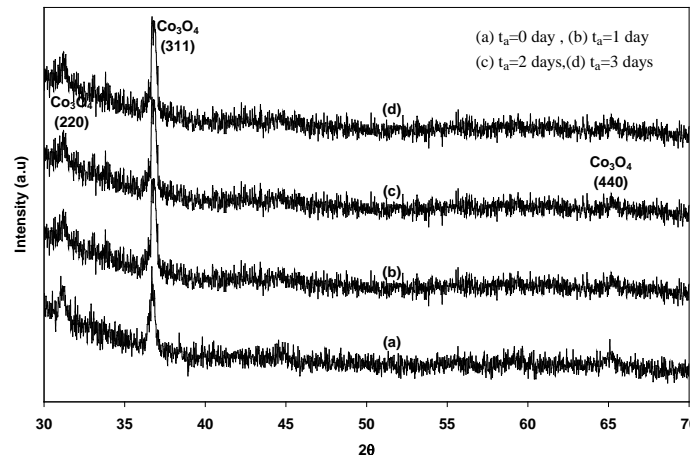


Figure 2:The XRD spectra of Co_3O_4 films with different sol aging times

Table 1:The thickness and crystallites sizes for Co_3O_4 thin films as a function of dipping time

Dipping time (min)	Thin film thickness (nm)	Mean diameter (nm)
0	595	30.32
3	600	32.31
5	605	40.33
7	607	53.8

As for the XRD patterns of the cobalt oxide films as a function of the sol aging, as presented in figure 2, one can easily notice that the growth of sol aging leads to the increase of the intensity of the major XRD peak, attributed to the (311) plane. Also, as the sol ages, the width of the same XRD peak increases, proving that the sizes of the

cobalt oxide crystallites increase.

Figure 3 presents the transmittance spectra of four cobalt oxide thin films, deposited by using the sol-gel technique, corresponding to 0, 3, 5 and 7 min dipping times of the substrate into the sol, respectively.

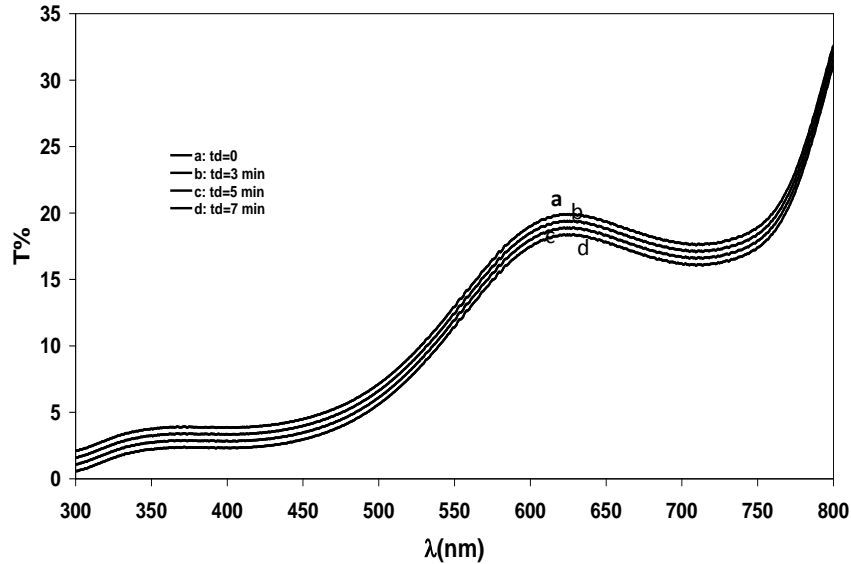


Figure 3: Transmittance spectra of cobalt oxide thin films, with different dipping times

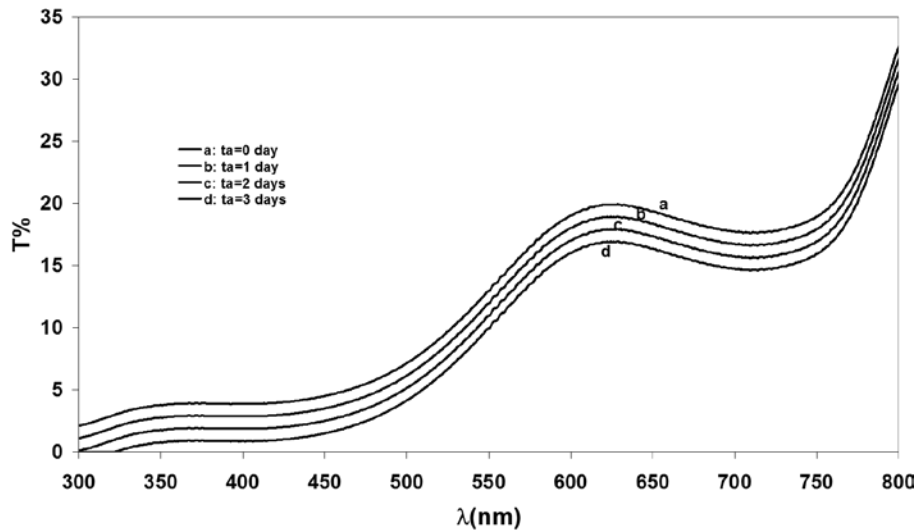


Figure 4: Transmittance spectra of cobalt oxide thin films, with different sol aging times

Figure 4 analyzes the influence of sol aging on the optical transmittance of the sol-gel-deposited cobalt oxide films. All the UV-visible transmission spectra of the cobalt oxide films from figures 3 and 4 present 2 absorption peaks. The first peak, from 430 nm, is typical for Co (2+) in the octahedral coordination, being ascribed to the ${}^4T_1 \rightarrow {}^4T_1(P)$ transition, while the second transmittance peak, noticeable at 730 nm, is due to the $O^{2-} - Co^{3+}$ charge transfer [12,13].

The values of the direct energy bandgaps for the analyzed cobalt oxide films were computed from the intercepts of the linear portions of $(\alpha h\nu)^2$ plotted against the photon energy, $h\nu$, according to formula (2), for $p = 1/2$ (see figure 5) and for $p=3/2$ (see figure 6). These absorption graphs are studied as a function of the sol aging time, t_a . The values of the energy bandgaps for both direct allowed and direct forbidden transitions, as obtained according to figures 5 and 6, are presented in Table 2.

Table 2: Variation of the optical bandgap with aging time for cobalt oxide films

t_a (days)	E_g (eV)	
	$p=1/2$	$p=3/2$
0	1.55	1.32
	2.08	1.41
1	1.50	1.33
	2.125	1.43
2	1.50	1.34
	2.15	1.48
3	1.50	1.35
	2.30	1.55

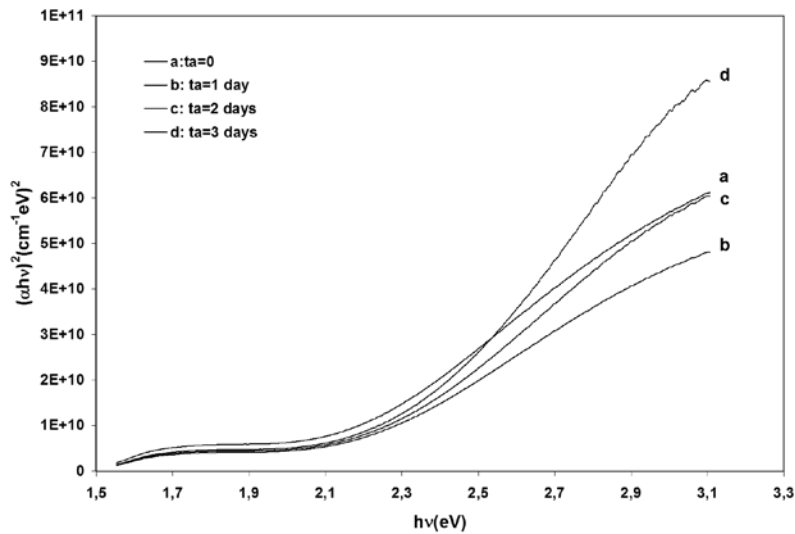


Figure 5:Plot of $(\alpha h\nu)^2=f(h\nu)$ for cobalt oxide films with different sol aging times

Each one of the absorption spectrum in figures 5 and 6 exhibit two linear portions, whose intercepts with the horizontal axis lead to two values for the energy bandgap, E_g of the studied films. Thus, Table 2 contains two values of E_g for each sol aging time, t_a and each type of direct optical transition. Both direct allowed and direct forbidden transitions occur within the analyzed cobalt oxide films.

The obtained energy bandgaps range between 1.5 eV and 2.3 eV, for direct allowed transitions, values which are

in good agreement with the values reported in the literature for the Co_3O_4 band structure [8].

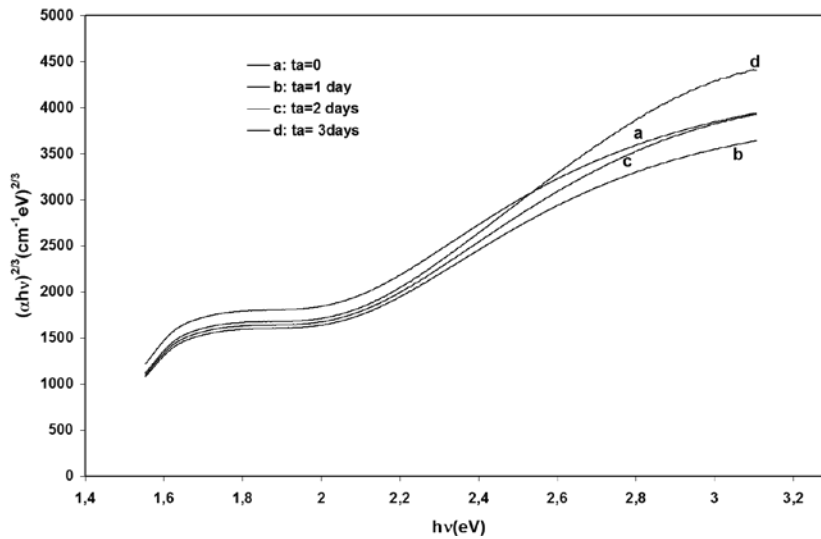


Figure 6: Influence of the aging time on the $(\alpha h\nu)^{2/3}=f(h\nu)$ dependence of sol-gel-deposited cobalt oxide films. Instead, the energy bandgap for direct forbidden optical transitions are, generally, smaller than for the allowed transitions, ranging between 1.32-1.35 eV and 1.43-1.55 eV, respectively, as corresponding to the two linear portions of the absorption spectra from Figure 6.

From Table 2, one can notice that, as the sol aging time, t_a increases, the optical energy bandgap generally increases, both for direct allowed and direct forbidden transitions.

Still, for direct allowed transitions, the energy bandgap towards lower values remains at 1.50 eV, no matter what is the sol aging time. Thus, it seems that the $\text{O}^{2-}-\text{Co}^{3+}$ charge transfer transitions are not influenced by sol aging and by the corresponding increase in crystallites sizes, while the ${}^4\text{T}_1 \rightarrow {}^4\text{T}_1(\text{P})$ transition of Co^{2+} needs higher energies for older sols and for improved crystallinity of the cobalt oxide films.

All the samples exhibit a similar optical behavior over the entire spectral range. There is a slight decrease in transmittance as the dipping time increases, due to the increase of the thickness of the analyzed films. As the 4 transmission spectra are identical, this is an indication of the fact that all 4 films have the same chemical composition.

4. Conclusions

Cobalt oxide thin films were deposited by means of the sol-gel dipping technique, by varying the dipping time and the sol aging time. The structure and the optical properties of the films were analyzed.

All the deposited films prove to be polycrystalline, with the (311) plane of Co_3O_4 predominating over other crystalline planes, formed within the samples, i. e. the (220) and (440) planes.

The mean diameter of the crystallites ranges from 30 nm to almost 55 nm in each of the analyzed films and increases with increasing dipping time of the substrates.

The aging time of the sol also influences the structure of the studied cobalt oxide films. As the sol ages, the crystallinity of the films improves and the size of the crystallites increases, as proved by the XRD spectra.

All the cobalt oxide films exhibit similar optical transmission spectra in the UV-Visible spectral range. As the sol aging time increases, the transmittance of the films decreases.

Two absorption peaks appear in the studied spectral domain, namely at 430 nm and at 730 nm, respectively, in good agreement with the reported cobalt oxide band structure [12,13]. These peaks correspond to the ${}^4T_1 \rightarrow {}^4T_1(P)$ transition for the Co (2+) ion, in the octahedral coordination and to the $O^{2-}-Co^{3+}$ charge transfer, respectively.

The studied cobalt oxide films exhibit both direct allowed and direct forbidden-type of optical transitions, with corresponding energy bandgaps between 1.32 eV and 2.30 eV, in good agreement with the literature.

The aging of the sol leads to an increase in the values of the energy bandgap for direct forbidden transitions. Instead, the direct allowed transitions happening at lower energies are not influenced by the age of the sol, while those at higher values increase as the sol ages. These findings prove that the age of the sol when performing the sol-gel deposition of cobalt oxide films influences more the values of the energy levels for the Co (2+) ion than those corresponding to the $O^{2-}-Co^{3+}$ charge transfer.

Thus, it was proved that the dipping time and the sol age may be chosen such as cobalt oxide films with different structures and different optical properties to be obtained by means of the sol-gel technique, which may prove useful for all sorts of applications.

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