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Structural characterization and optical properties of Co_3O_4 and CoO films

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Thin-film coatings based on cobalt oxides are obtained. For depositing cubic spinel Co_3O_4 and CoO films the sol-gel dip-coating technique was used. The as-deposited films were subjected to different thermal treatments in air and in reducing atmosphere (H_2/N_2), respectively. Optical absorption spectroscopy, X-ray diffraction and atomic force microscopy (AFM) were used to characterize the samples. The Swanepoel method was employed for the study of the films optical constants as a function of wavelength. By XRD studies it was established that the annealed films become polycrystalline. The films exposed in air consist in Co_3O_4 phase, while the films annealed in reducing atmosphere (H_2/N_2) exhibit the CoO phase. AFM studies showed uniform films with smooth surface. By exposing the film to H_2/N_2, the average rugosity increases ten times. After treatment, the cobalt oxide films transmittance values decrease. The decrease is more meaningful when the films are exposed in reducing atmosphere. The UV-VIS spectra of the films exposed in air present an absorption peak at λ= 730 nm, which corresponds to a charge transfer ligand-metal: $O^{2-} \rightarrow Co^{3+}$. The peak which corresponds to λ= 690 nm is due to Co^{2+}. These transitions confirm the existence of Co_3O_4. Concerning the films annealed in reducing atmosphere (H_2/N_2), the band at 594 nm which appears in the spectra is typical for Co^{2+} in octahedral coordination and ascribed to the $^4A_2 \rightarrow {}^4T_1(P)$ transition. The refraction index presents a normal dispersion, the films exposed in forming gas having higher values than the films exposed in air. The films annealed in a reducing atmosphere feature only direct transitions, representing an internal oxido-reduction process $Co^{3+} \rightarrow Co^{2+}$. The films exposed in air present both direct and indirect transitions. Co_3O_4 films present an allowed direct interband transition of 1.4-1.5 eV and 2.18-2.23 eV, respectively, while CoO films have an optical band gap energy of 2.2-2.8 eV.

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Keywords: Sol-gel, Cobalt oxide, Optical constants, Optical band gap

1. Introduction

Cobalt oxide is a metal oxide material with many industrial applications such as thin film catalysis, gas and humidity sensors[1-2], electrochemical capacitors for high power devices in energy storage systems[3], heterogeneous catalysis for NO decomposition[4] etc.

This paper reports the influence which different annealing atmospheres have on the structural properties of cobalt oxides based films and implicitly on their optical properties.

2. Experimental procedure

For depositing cubic spinel Co_3O_4 and CoO films, the sol-gel dip-coating technique was used.

The films were obtained by immersing the glass slides into cobalt colloidal solution. After immersion into the cobalt solution, samples were dried at 100°C. By heating the samples at 300°C, the dried gels passed in to a solid oxide film. The withdrawal speed and the number of dipping-heating cycles (number of layers) were kept constant. The obtained cobalt oxide films were heated at 500ºC in different annealing atmospheres: a) in air; b) in air followed by heating in forming gas (H_2/N_2) and c) only in H_2/N_2.

X-ray diffraction and atomic force microscopy (AFM) were used to characterize the samples. The X-ray diffraction was performed using a Rigaku diffractometer (CuKα, λ=1.5418Å). The morphology analyses were carried out by using an atomic force microscope.

The sizes of cobalt oxide particles determined by using Scherer's formula were compared with those measured by atomic force microscopy.

The optical transmittance was measured using a UV-VIS-NIR double beam spectrophotometer in the wavelength range from 300 to 800 nm.

3. Results and discussion

By XRD studies it was established that the annealed films become polycrystalline.

We can notice that films exposed 4h in air (Fig.1a) and those heated 4h in air followed by exposing them 1h in forming gas (Fig.1b) present a major peak at 2θ=39.58°, which indicates the existence of Co_3O_4 as disperse phase. This peak corresponds to (311) plane.

The mean crystallite size, D_m, grows significantly from 14.47 nm (a) to 32.16 nm (b). The value of D_m will grow with 7 -10 nm if the film is exposed only in air for 5 hours.

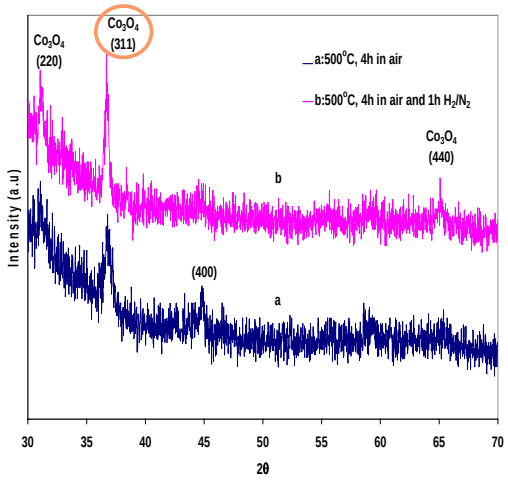

Fig.1 XRD patterns of cobalt oxide films annealed at 500ºC: a) 4h in air ; b) 4h in air followed by heating 1h in forming gas

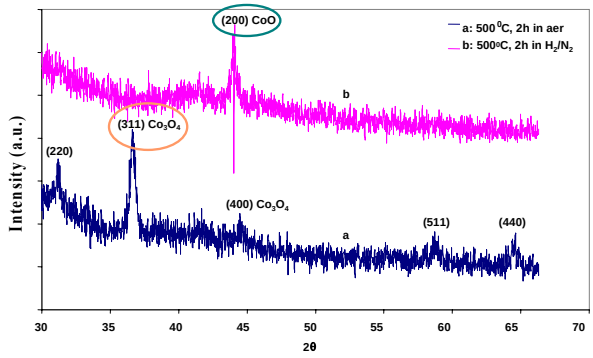

Fig. 2. XRD patterns of cobalt oxide films annealed at 500ºC: a) 2h in air; b) 2h in H_2/N_2.

Fig. 2 presents the XRD patterns for two films, having the same deposition parameters, which were annealed: a) 2h in air; b) 2h in H_2/N_2. The XRD patterns revealed that the films annealed in reducing atmosphere (H_2/N_2) consist of CoO phase. The preferential direction of crystallization is along the (200) plane.

If the temperature of the treatment is less than 500^0C, all the films are amorphous or the mean crystallite size is too small to be detected by XRD analysis.

The AFM pictures presented in fig.3 and fig. 4 belong to a film with 6 layers, which wase deposited with a withdrawal speed of v=11cm/min from a 36.8 g/l cobalt colloidal solution. In fig.3, the AFM picture was made after the film was treated at 500^0C, for 4h in air. The AFM picture from Fig.4 presents the film after being exposed 4h in air followed by heating 1h in forming gas, at the same temperature. In the first case the average rugosity, R_m was 1.52 nm for a mean crystallite size, D_m , of 24.53 nm, while in the second situation R_m=10.52 nm for D_m=32.16 nm.

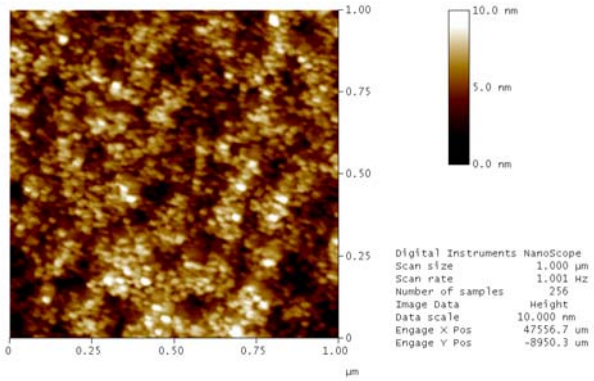

Fig.3 AFM picture of a film treated at 500^0C, 4h in air (c=36.8g/l, v=11cm/min, 6 layers).

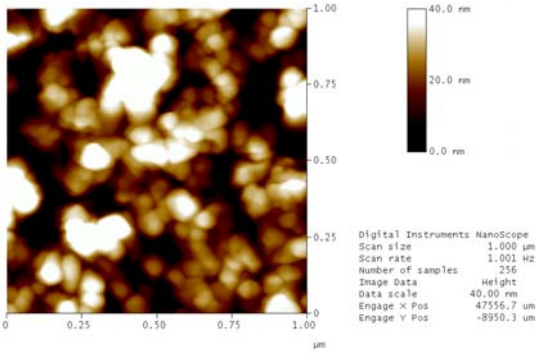

Fig. 4. AFM picture of a film treated at 500^0C, 4h in air followed by heating 1h in forming gas (c=36.8g/l, v=11cm/min, 6 layers)

The average rugosity increases ten times when the film is heated in forming gas (H_2/N_2).

We assume that hydrogen gets easily into the crystals' inner space due to it's higher diffusion coefficient. This generates dislocations and implicitly an increased mean roughness.

Generally, the surfaces of the films are uniform, without cracks.

Fig. 5 shows the influence of thermal treatment on the transmission spectra of cobalt oxide films.

After treatment, the cobalt oxide films transmittance values decrease. The decrease is more meaningful when the films are exposed in reducing atmosphere. The UV-VIS spectra of the films exposed in air present an absorption peak at λ= 730 nm, which corresponds to a charge transfer ligand-metal: $O^{2-} \rightarrow Co^{3+}$. The peak which corresponds to λ= 690 nm is due to Co^{2+}. These transitions confirm the existence of Co_3O_4.

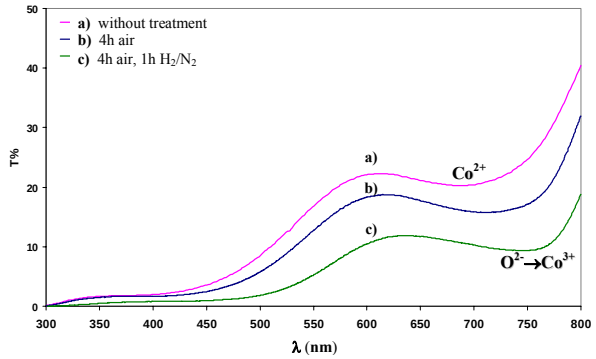

Fig. 5 Influence of thermal treatments on the transmission spectra of cobalt oxide films

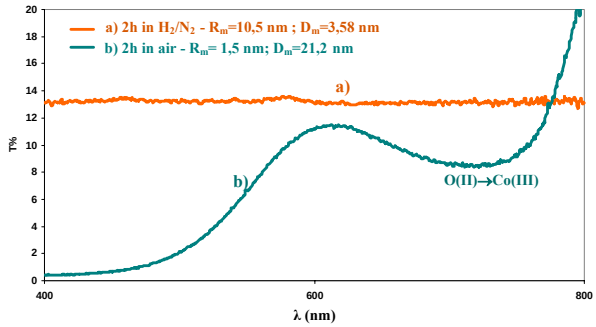

Fig.6 Thermal treatment influence on the transmittance spectra of cobalt oxide films (R_m-mean rugosity, D_m-mean crystallite size)

By exposing the film only to H_2/N_2, the average rugosity increases ten times. This is reflected in the absence of the absorption peaks (Fig.6).

In order to determine the optical band gap values, the optical data were analyzed using the Tauc law [8]:

$$\alpha h\nu = A\left(h\nu - E_g\right)^p \qquad (1)$$

where $\mathbf{E_g}$ is the optical band gap, **A** a constant and **p** a constant which depends on the kind of optical transition. Thus p is 1/2 for direct allowed transitions and 3/2 for forbidden transitions.

The direct bandgaps were determined from the plots of $(\alpha h\nu)^2$ vs. $h\nu$ (Fig.7). The intercepts of the two straight line portions give energy gap values.

For Co_3O_4 films, the values are in the range 1.4—1.5 eV for lower energy side region and 2.18-2.23 eV for higher energy side region, in agreement with the reported Co_3O_4 band structure [9].

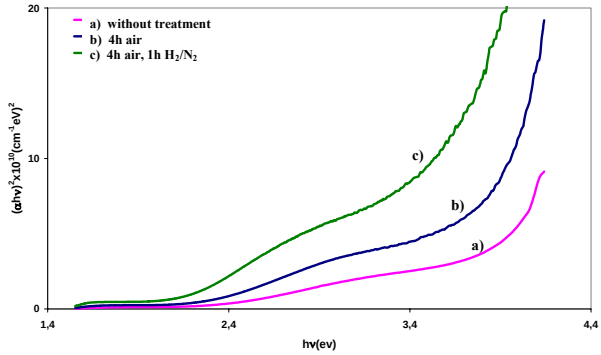

Fig.7 Plot of $(\alpha h\nu)^2=f(h\nu)$ for cobalt oxide films prepared in the same conditions, but undergoing different thermal treatments

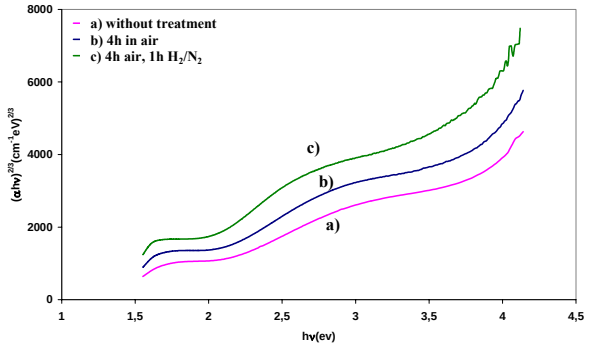

Fig.8 Plot of $(\alpha h\nu)^{2/3}=f(h\nu)$ for cobalt oxide films prepared in the same conditions, but undergoing different thermal treatments

Variation of $(\alpha h\nu)^{2/3}$ vs. $h\nu$ (Fig.8) was also studied to highlight direct forbidden transitions. The two straight line portions have the intercepts in the range of 1.25-1.3eV respectively 1.5-1.6eV, suggesting direct forbidden transitions occurring at these energies.

For the evidence of indirect transitions, the following equation [9,10] was used:

$$\alpha = \frac{B\left(h\nu - E_g^{'} \pm E_p\right)^p}{h\nu} \qquad (2)$$

where $\mathbf{E}_g^{'}$ is the indirect energy gap, $\mathbf{E_p}$ the photon energy and **B** is a constant. The constant p is 2 for indirect allowed transitions and 3 for forbidden transitions, respectively.

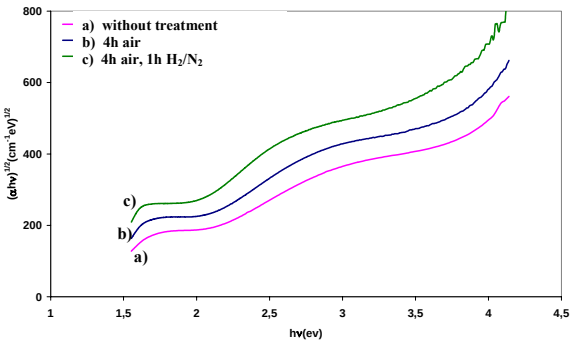

Fig.9 Plot of $(\alpha h\nu)^{1/2}=f(h\nu)$ for cobalt oxide films prepared in the same conditions, but undergoing different thermal treatments

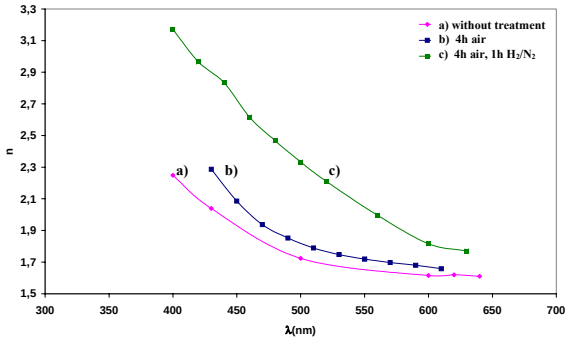

Fig.10 The refraction index dispersion for cobalt oxide films prepared in the same conditions, but undergoing different thermal treatments

The plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (Fig.9) gives intercepts at about 1.2 eV respectively 1.3 eV, giving the values E′g= 1.25 -1.3eV and E_p=0.05eV for an indirect allowed transition. We can conclude that all these films present both direct and indirect transitions.

CoO films present only an allowed direct interband transition of 2.2-2.8 eV. No indirect transitions were observed.

From the transmittance spectra the refractive index, using Swanepoel method, was determined. The refraction index presents a normal dispersion, the films exposed in forming gas have higher values than the films exposed in air.

4. Conclusions

By XRD studies it was established that the annealed films become polycrystalline. The films exposed in air consist in Co_3O_4 phase, while the films annealed in reducing atmosphere (H_2/N_2) in CoO phase.

The UV-VIS spectra also confirm the existence of Co_3O_4 or CoO.

Co_3O_4 films present an allowed direct interband transition of 1.4-1.5 eV and 2.18-2.23 eV, respectively, while CoO films have optical band gap energy of 2.2-2.8 eV. The films annealed in H_2/N_2 feature the highest refraction index values.

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