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Effects of Various Concentation Molarities on the Optical and Dispersion Parameters of Nanostructured Cobalt Oxide Layers by SP Process

Soufiane Benhamida [1], Fayçal Baira [2], Hazem Bouraoui [3,4], Yamina Benkrima[5]

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Abstract: Nanostructured Cobalt oxide (Co_3O_4) layers were made by using spray pyrolysis (SP) technique, the aqueous solution of hydrated cobalt chloride salt ($CoCl_2 \cdot 6H_2O$) were used as source of cobalt. The films were deposited onto the glass substrates kept at 400ºC. The impacts of molar concentration varied from (C= 0.2 to 0.3 mol/l) of the starting solution on the optical and dispersion parameters of cobalt oxide layers were studied. It was found from the optical transmission that the maximum transmittance was observed for the sample prepared at molar concentration of 0.3mol/l. In addition, the refractive index and extinction coefficient, were calculated.

***Key words**: Cobalt oxide; Thin films; spray pyrolysis; Optical properties, dispersion parameters*

1. Introduction

Cobalt oxide (Co_3O_4) is among the most extensively researched transition metal oxides for many scientific applications. Cobalt oxide possesses numerous industrial applications, including its use as a solar selective absorber, a catalyst in the hydrocracking of crude fuels, a pigment for glass and ceramics, a catalyst for oxygen evolution and reduction reactions, and in the glass sector for producing colored glass [1-3]. The widely recognized catalytic qualities may result from the lowering of activation energies for the chemisorption of gas molecules, which significantly enhances gas sensitivity and lowers operational temperatures. It is extensively utilized as an electrochromic material, electrochromic anode, and supercapacitor [4,5]. Cobalt oxide is a highly flexible ceramic material, recognized as a p-type antiferromagnetic oxide semiconductor with the highest Curie temperature, Tc = 1396 K. This oxide is typically denoted by its chemical formula Co_3O_4; however, it is, in reality, non-stoichiometric [6,7]. Cobalt exhibits a lower affinity for oxygen than iron, although a higher affinity than nickel [8]. It possesses three notable polymorphs: cobaltous oxide (CoO), cobaltic oxide (Co_2O_3), and cobaltosic oxide or cobalt cobaltite (Co_3O_4). Numerous papers in the literature document the manufacture of cobalt oxide films by various physical and chemical processes. Methods such as spray pyrolysis [9], reactive pulsed magnetron sputtering [10], chemical vapor deposition (CVD) [11], pulsed laser deposition (PLD) [12], sol-gel process [13], and electrodeposition (ED), applied to various substrates[14]. Spray pyrolysis offers numerous advantages, including cost-effectiveness, versatility, the capacity to produce porous and nanostructured thin films, and suitability for large-area deposition [15]. This study utilizes the spray pyrolysis method to fabricate nanostructured cobalt oxide (Co_3O_4) layers on a glass substrate. In the present work, nanostructured cobalt oxide thin films have been prepared by SP technique at an optimized substrate temperature (400ºC) with precursor solution prepared at different molar concentration, the effect of concentration molarity on the optical and dispersion parameters were studied.

1 Faculty of Mathematics and Material Sciences, Radiation and Plasma and Surface Physics Laboratory (LRPPS), University of Kasdi Merbah Ouargla, 30000, Ouargla, Algeria.

2 Department of sciences and technology, Faculty of technology, University of Batna 2, Alleys 53, Constantine Avenue. Fésdis, Batna 05078, Algeria.

3 Laboratoire de Cristallographie, Université Mentouri, Constantine, Algérie.

4 Univ. Ouargla, Fac. des Mathématiques et Sciences de la Matière, route de Ghardaia, Ouargla 30000, Algeria.

5 Ecole Normale Supérieure de Ouargla, 30000, Algeria.

** Corresponding author. Email: benhamidas9@gmail.com*

2. Experimental procedure

2.1. Synthesis and characterization of the layers

Cobalt oxide layers were prepared from solution of hydrated cobalt chloride $CoCl_2 \cdot 6H_2O$ dissolved in 30 ml of double-distilled water, with different molar concentrations 0.2and 0.3M. the mixture was agitated at 50°C with a magnetic stirrer for thirty minutes to achieve a homogeneous solution. The final solution was then sprayed in an atmospheric setting onto heated surfaces that were 400°C. The distance from the nozzle to the substrate was kept at 12 cm, with the solution being sprayed at a flow rate of 2 ml/min. The substrates comprised tiny glass slides measuring 75×25×1.1 mm³ (R217102). Before the deposition process, glass substrates were subjected to a standard cleaning procedure involving a 10-minute rinse in acetone and distilled water, followed by drying with compressed air. Subsequent to deposition, the films were allowed to cool gradually to room temperature. Spray deposited films are characterized by using We used the Cray 100 Agilent Technologies to measure the optical transmittance spectra of all prepared films in the spectral range of 300–800 nm.

3. Result and discussions

3.1 Optical and dispersion parameters

The optical invertigation of cobalt oxide Co_3O_4 layers were analyzed using UV-Vis-NIR spectrometer. The optical transmission spectra of prepared layers with different molar concentration 0.2 and 0.3Mare shown in Fig. 1. As can be seen, the Co_3O_4 samples exhibits at higher concentration (0.3M) shows an average optical transmittance of about 81.24% in the visible region . however the sample prepared at (0.2M) has an average optical transmission around 67.31% .This is can be explicated by a less light scattering of this film due to its smoothest surface [15]. Conversely, the region of elevated absorption aligns with the fundamental absorption (λ<400nm) in cobalt oxide layers, attributed to interband electronic transitions. This results unequivocally demonstrate that this material is suitable for use as a transparent oxide in solar cells.

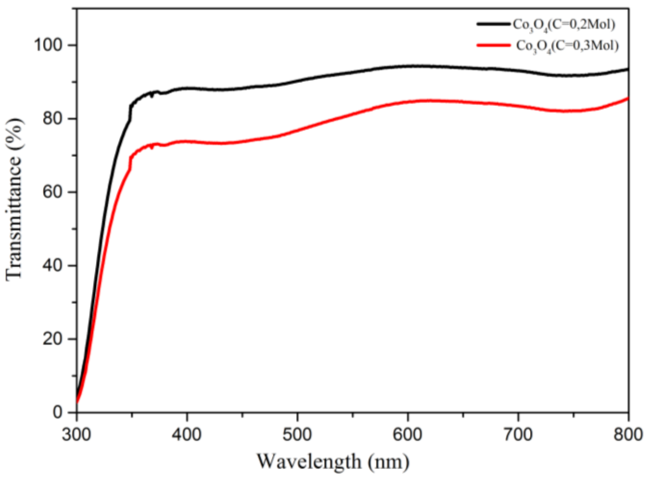

Fig. 1: transmittance spectra of cobalt oxide layers prepared at different molar concentration

The absorption coefficient has been calculated from Lambert's formula [16]:

$$\alpha = \frac{\ln(1/T)}{d} \quad (1)$$

where T and d are the transmittance and thickness of the films respectively.

The Optical energy gap E_g and absorption coefficient α are related from the Tauc's relation [17]:

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

where α is the absorption coefficient, ($h\nu$) is the photon energy, and A is a constant and n is the constant that is equal to 2, 1/2, 2/3 and 1/3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. The E_g values were evaluated by plotting $(\alpha h\nu)^2$ against ($h\nu$) and extrapolating the linear portion of the curve to the energy axis at $\alpha = 0$. Fig. 2 shows the plot of $(\alpha h\nu)^2$ vs. ($h\nu$); the corresponding E_g values are presented in Table 1. The energy gap values obtained range from 3.92 to 3.95 eV for samples generated with concentrations of C = 0.2 and C = 0.3 mol/l, respectively. The augmentation of the band gap in cobalt oxide films, as the concentration rises from

C=0.2 to C=0.3 mol/l, can be elucidated by the widening of the band gap [16].

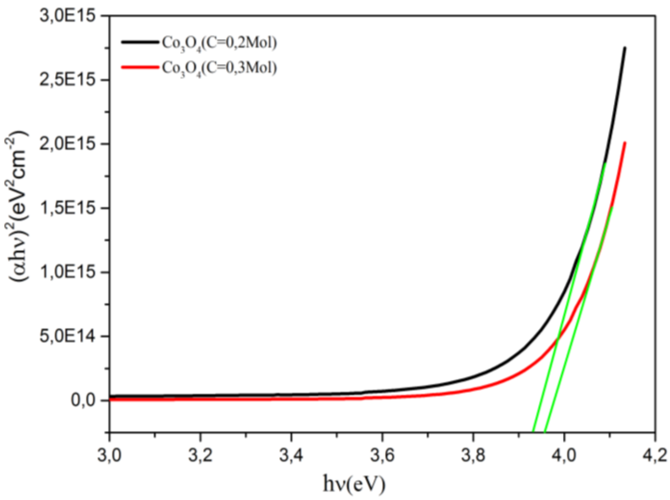

Fig.2: Estimation of band gap energy (Eg) from Tauc's relation of cobalt oxide layers prepared at different molar concentration

Optical dispersion parameter such as the index of refraction (n) and extinction coefficient (k) plays a significant function in the optoelectronic and transparent electrode applications. The values of (n) and (k) of the prepared layers were determined by the following equations [17]:

$$n = \left(\frac{1-R}{1+R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{3}$$

and

$$k = \frac{\alpha\lambda}{4\pi} \tag{4}$$

Where (λ), (R), (α), and (k) are the wavelength, the reflectance, the absorption coefficient, and the extinction coefficient, respectively. Figure 3 shows the appearance of the refractive index of cobalt oxide prepared with different concentrations over the wavelength range from 300 nm to 800 nm. As shown, the refractive index spectra exhibit a sharp drop near 400 nm and then take on a value that is almost independent of the wavelength in the visible and near-infrared regions. The value of the refractive index of cobalt oxide layers prepared at the wavelength (550 nm) is indicated in the table1.It can be observed that the thin films prepared under experimental conditions (C = 0.3 mol) or n = 1.84, exhibit a higher value compared to the thin films prepared under experimental conditions (C = 0.2 mol) or n = 1.65. the variation in the refractive index is directly related to the nature of the surface of the deposited material or when it is affected by the speed of light propagation as it passes through the thin layer [18].

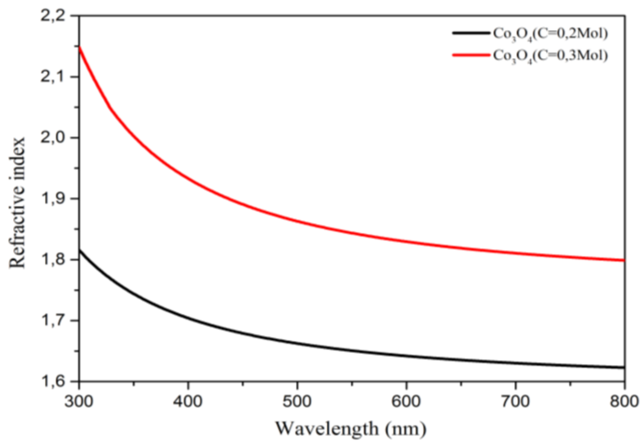

Fig. 3: refractive index as function of wavelength of cobalt oxide layers prepared at different molar concentration

The extinction coefficient of cobalt oxide synthesized with varying concentrations is shown to vary with wavelength from 300 nm to 800 nm in Figure 4. The extinction coefficient is significantly influenced by wavelength in the ultraviolet range, while it remains rather stable in the visible and near-infrared regions. 400 to 800 nanometers. It is noted that throughout all layers, the extinction coefficient k diminishes with increasing wavelength, attaining relatively low values in the visible and near-infrared regions. The extinction coefficient typically diminishes as thickness increases. The minimal values within the 400-800 nm range clarify the transparent characteristics of the synthesized films [19].

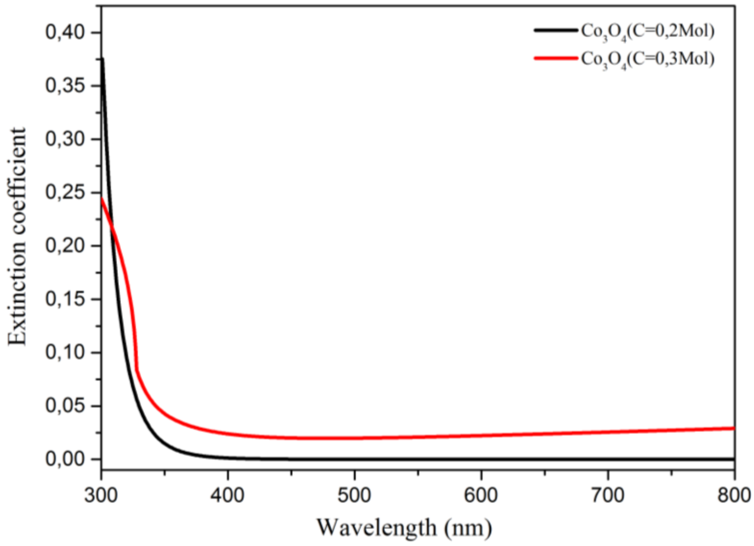

Fig. 4: Extinction coefficient as function of wavelength of cobalt oxide layers prepared at different molar concentration

4. Conclusion

Cobalt oxide (Co_3O_4) thin layers were successfully prepared by using spray pyrolysis route on a glass slide at 400°C from aqueous solution of hydrated cobalt chloride ($CoCl_2{\cdot}6H_2O$) as source of cobalt. The effect of molar concentrations on optical and dispersion parameter were investigated in this work. The optical invertigation of cobalt oxide Co_3O_4 layers were analyzed using UV-Vis-NIR spectrometer. The pepared films exhibits transmittance value of about 81.24% in the visible range at concentration (0.3M) however the sample prepared at (0.2M) has an average optical transmission around 67.31%. the gap energy was increased from 3.92 to 3.95 eV as molar concentation increases. Furthermore, the refractive index of the films was found to vary strongly with concentration. These results suggest that present films may act as potential candidates for the for optoelectonic and supercapacitor applications.

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