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Optical Properties of Co_3O_4 Films Deposited by DC Electrochemical Method

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Abstract

The Co_3O_4 films are prepared on thoroughly cleaned stainless steel substrates by using electrochemical deposition method with $Co(NO_3)_2.6H_2O$ as Co precursor solution. The resultant films are characterized by using XRD, UV-Visible spectroscopy and FTIR spectroscopy and scanning electron microscopy. The characterization studies showed that the resultant films are single phase cubic-spinel Co_3O_4. The resultant films showed the comparble values of absorptance (α) = 0.91 and emittance (ε) = 0.08 as compared to reported data. It is found that, the optical properties of Co_3O_4 films strongly depend on the concentration of $Co(NO_3)_2.6H_2O$ in deposition bath. The films deposited in present work are found to have good prospective for selective solar absorption coatings.

Keywords: Co_3O_4 films; DC eletrochemical depsoition; Optical properties.

Introduction

Due to increased interest in solar energy applications there is a fast development of spectrally selective surfaces with high absorptance across the solar spectrum and low emmittance for longer wavelengths relevant to thermal eradication [1]. Low cost, ease in mass production, stability at operating temperatures and good resistance to thermal shocks, oxidation, UV radiation, humidity & handling are the properties of practical solar selective coating. For such applications, p-type antiferromagnetic Co_3O_4 is one of the promising transition metal oxide semiconductor materials [2]. For many industrial applications: high-temperature solar selective absorbers, catalyst in hydrocracking process of crude fuels, pigment for glasses & ceramics, catalyst for oxygen evolution & reduction reaction, electrochromic material etc. the Co_3O_4 is a good candidate [3].

Owing to having number of parameters for optimization of properties and controlling the surface morphology of films as compared to other methods, electrochemical deposition is versatile method for preparation of films [4-5]. It is very simple and cheap method of deposition of films [5]. For Co_3O_4 films, the highest values of absorptance (α) in the range of 0.92 - 0.93 are reported in literature [6-8]. The electrochemical deposition of nanowired Co_3O_4 films on glass substrates is reported in literature [5]. It is well known that properties of films are susceptible to deposition method and its parameters. The materials of film material can be tailored in terms of structure, grain size, resistivity and band gap energy [5]. In view of this, the main objective of present work was to use novel electrochemical deposition method for the preparation of Co_3O_4 films with better optical properties [9]. The results obtained related to the optical properties of electrochemically deposited Co_3O_4 films are presented in this communication.

Experimental Work

Initially, $Co(NO_3)_2.6H_2O$ (0.1 M) and H_3BO_3 (0.12 M) were dissolved in 250 ml of double distilled water (DDW) and solution was filtered by using Whatman 41 filter paper. The pH of solution was maintained at ~ 4.5 by adding NaOH / HCl in solution. The stainless steel substrates [area = 4 cm^2, thickness = 0.5 mm] were cleaned thoroughly by using procedure: (i) dipping in a solution containing 50 % HNO_3 and 10 % chromium at room temperature (RT) for 30 min., (ii) dipping in a solution containing 10 % H_2SO_4 at RT for 10 min., (iii) rinsing with acetone, (iv) cleaning with soap solution in double distilled water, (v) rinsing with acetone/alcohol by dip method and finally (v) cleaning with dilute detergent and warm water. After these treatments, the SS substrates were kept in acetone prior to the deposition of films.

The cobalt based films were deposited on SS substrates by using home-built DC electrochemical deposition system at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 M concentration of $Co(NO_3)_2.6H_2O$ in deposition bath with the parameters: (a) cathode-anode distance = 2.5 cm, (b) current density = 10 mA/cm^2 and (c) deposition time = 8 min. The films were washed gently in DDW and then heated at 350 ^oC for 2 hr. The films prepared at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 M concentration of $Co(NO_3)_2.6H_2O$ were identified as ESN1, ESN2, ESN3, ESN4, ESN5, ESN6 and ESN7 respectively. The X-ray diffraction (XRD) patterns of films were recorded by using X-ray diffractometer (Bruker D8 Advance Machine, Germany CuKα radiation λ = 1.5418 Å) for phase analysis. Fourier transform infrared spectra of films recorded by using FTIR spectrophotometer (JASCO make, Model: V6100A, FTIR-8400, Shimadzu, Japan) were used to obtain solar thermal emittance (ε) of films. The UV-Visible spectra recorded by using JASCO Model: V670 spectrometer were used to obtain absorptance (α) and band gap (E_g) values of films.

Results and Discussions

Figures 1 gives the XRD patterns for the films: ESN1 to ESN7. All the diffraction patterns of different films are found to be similar to each other. All the peaks of various XRD patterns are perfectly indexed to the Co_3O_4 phase with cubic spinel symmetry given in JCPDS data file for Co_3O_4 [JCPDF-76-1802]. The peaks corresponding to other cobalt oxide phases [1- 4] are not observed in all the XRD patterns. The values of lattice parameter (a_o) calculated from (400) reflection plane for the XRD patterns of ESN7 is found to be 8.061 Å. This value of 'a_o' is found to be very close to the reported value of 8.084 Å for Co_3O_4 phase with cubic spinel symmetry [5 - 9]. All above observations clearly indicate the formation of single phase Co_3O_4 with cubic spinel symmetry in the films deposited by using $Co(NO_3)_2.6H_2O$ precursor on both SS substrates and heated at 350 °C for 2 hr. This confirms the purity of materials of all the films

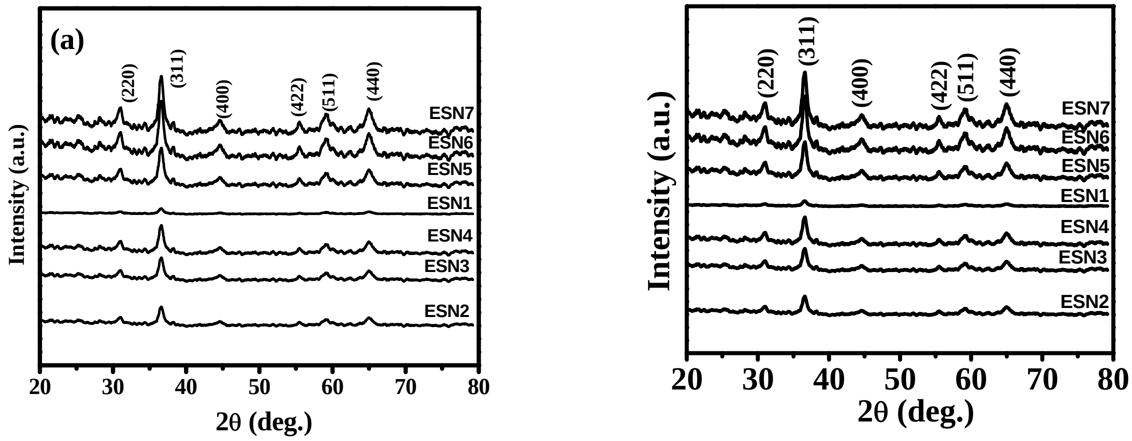

Figure 1. XRD patterns of ESN1 to ESN7 films

Figure 2 gives the Fourier transform infrared spectroscopy (FTIR) spectra for ESN1 to ESN7 films . Similar observations are noted for the films prepared on SS substrates for the different molar concentration of $Co(NO_3)_2$ precursor in deposition bath. The bands centered around 507 cm^{-1} and 584 cm^{-1} corresponding to the FCC CoO and hexagonal CoO(OH) respectively [11-12] are not found in all the spectra. These bands are likely to be associated with the Co ion in octahedral holes in an oxygen octahedral environment.

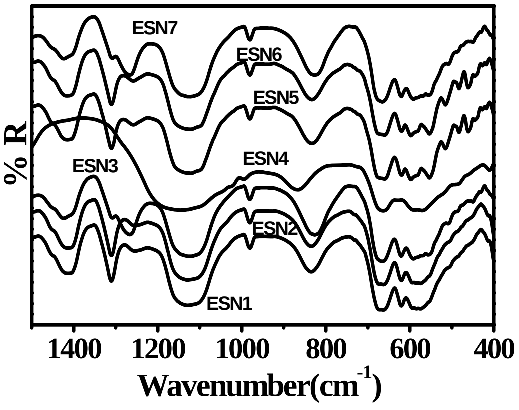

Figure 2. FTIR spectra of ESN1 to ESN7 films

The strong peaks centered around 550 cm^{-1} and 665 cm^{-1} and characteristic of spinel Co_3O_4 are clearly seen in all the spectra. This indicats the formations Co_3O_4 phase in all the as-heated films [12-13]. These 2 distinct bands originate from the stretching vibrations of the Co - O bonds [14]. The peak around 550 cm^{-1} is associated with the OB_3 vibration in the spinel lattice [B denotes the Co^{3+} in an 0Ctahedral hole]. The peak around 665 cm^{-1} is attributed to the ABO_3 vibration [A denotes the Co^{2+} in a tetrahedral hole] [14]. These observations clearly indicate the formation of single phase Co_3O_4 with cubic spinel symmetry in all as-heated films.

To understand the surface morphology of as-heated films, the scanning electron microscopy (SEM) study is undertaken. Figure 3 gives the scanning electron microphotographs for the ESN1 to ESN7 films. The following observations are noted from SEM microphotographs.

(i) different morphology: spherical (in case of ESN5 film), flakes-liquid type sintering (in case of ESN2, ESN4, ESN6 and ESN7 films), spherical + rod + varied shaped type (in case of ESN1, ESN3 films) are obser

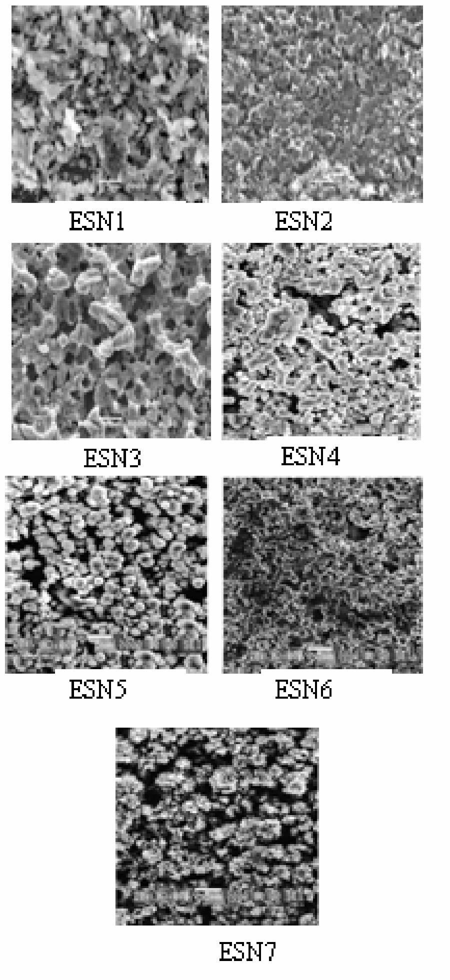
ESN1 ESN2
ESN3 ESN4
ESN5 ESN6
ESN7

Figure 3 SEM images for the resultant ESN1 to ESN7 films

(ii) Mixed soft and hard agglomeration nature is observed in all the films.

(iii) Sizes of particles are observed generally in the range of 1 - 3 μm.

(iv) The particle size distribution is nearly uniform in case of the films having spherical morphology.

(v) Voids are observed in all films deposited indicating thereby the low densification at surface of all as-heated films.

Figure 4 gives the UV-Visible spectra for ESN1 to ESN7 films. The absorptance (α) was calculated by using the formula,

$$((T) = (\int_{,}(\min{}^{1}(\max [[1 - r("(" ,T)]I("(" ,T)d" ("])/(\int [I("(" ,T)d" ("]) \quad \text{-- (1)}$$

where,

I (λ,T) = intensity of black body radiation at wavelength λ and

T = Temperature.

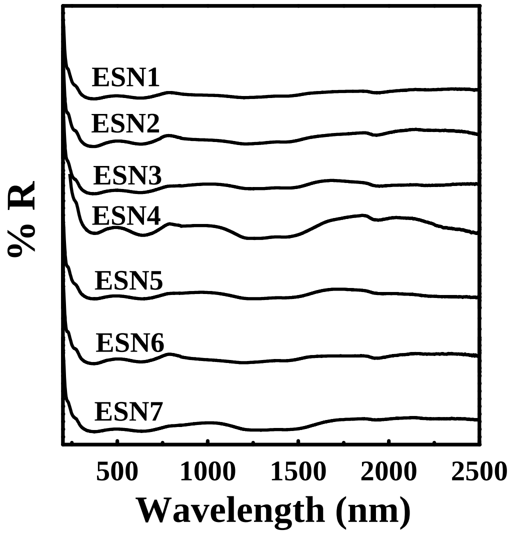

Figure 4. UV-Visible spectra for ESN1 to ESN7 films

The data for absorptance (α) given in Table 1 indicates that the absorptance (α) is increasing with the molar concentration of $Co(NO_3)_2$. The highest value of absorptance (α) = 0.91 is noted for ESN5 film at 0.5 M concentration of $Co(NO_3)_2$. This value of absorptance (α) is comparble with the reported data (α = 0.92-0.93) [6 - 8] and obtained for the film deposited at lower molar concentration of H_3BO_3 (~ 0.12 M) as compared to literature [15]. The FTIR spectra were used for the calculation of emittance (ε) of resultant films. The values of emittance (ε) of resultant films were calculated by using the formula,

$$((T) = (\int_{,}(\min{}^{1}(\max [[1 - r("(" ,T)]I("(" ,T)d" ("])/(\sigma T^{1}4) \quad \text{--- (2)}$$

where, $I(\lambda,T) = C_1/(\lambda^5[e^{(C_2/\lambda T)} - 1])$,

$\sigma = 5.6696 \times 10^{-8}$ wm^{-2}K^{-4},

$C_1 = 3.7405 \times 10^8$ Wμm^{4}m^{-2} and

$C_2 = 1.4387 \times 10^4$ μm K.

The ε (Table 1) is found to be decreasing with increasing the molar concentration of $Co(NO_3)_2$. The values of ε are found to be in the range of 0.080 - 0.170 for ESN1 to ESN7 films. The minimum value of ε is found to be 0.080 for ESN5 film (with $\alpha = 0.91$). This value of ε is found to be smaller than the reported data [6 - 8]. The UV-Visible spectra for different films (Figure 4) were analyzed by using the equation,

$$\alpha = (\alpha_o/h\nu)[(h\nu - E_g)]^n \qquad \text{--- (3)}$$

where, α_o = constant, n = 1/2 and 2 for direct and indirect transitions respectively [16]. Figure 5 gives the variation of $(\alpha h\nu)^2$ with hν for ESN1 to ESN7 films. The values of band gap energies (E_g) are obtained by extrapolation of the straight-line portions of the plots to zero absorption coefficients (Table 1) and are found to matching with the reported data [17] for Co_3O_4 phase.

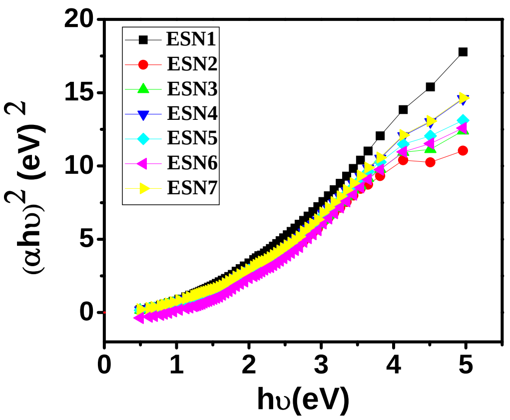

Figure 5. $(\alpha h\nu)^2$ vs. hν variation for ESN1 to ESN7 films

Table 1. Data for absorptance (α), emittance (ε) and Band gap energy for ESN1 to ESN7 films

Molar conc. of $Co(NO_3)_2$	Film name	α	ε	E_g (eV)
0.1	EUN1	0.810	0.170	1.462
0.2	EUN2	0.820	0.150	1.487
0.3	EUN3	0.830	0.130	1.500
0.4	EUN4	0.840	0.110	1.552
0.5	EUN5	0.910	0.080	1.579
0.6	EUN6	0.830	0.100	1.590
0.7	EUN7	0.830	0.090	1.610

Conclusions

The optical properties of Co_3O_4 films deposited on stainless steel substrates by using DC electrochemical method depend on $Co(NO_3)_2.6H_2O$ molar concentration. The films deposited at 0.5 M concenatation of $Co(NO_3)_2.6H_2O$ showed the better values of absorptance (α) = 0.91 and emittance (ε) = 0.08.

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References

[1] A. Avila G., E. Barrera C., L. Huerta A., and S. Muhl ‘‘Cobalt oxide films for solar selective surfaces obtained by spray pyrolisis,’’ Sol. Eng. Mater. & Sol. Cells, vol. 82, issue 1-2, pp. 269 - 278, 2004.

[2] P. S. Patil, L.D. Kadam, and C. D. Lokhande, “Studies on electrochromism of spray pyrolyzed cobalt oxide thin films,’’ Sol. Eng. Mater. & Sol. Cells, vol. 53, issue 3 - 4, pp. 229 -234, 1998.

[3] G. E. McDonald, “Preliminary study of a solar selective coating system using black cobalt oxide for high temperature solar collectors,’’ Thin Solid Films, vol. 72, issue, pp. 83 - 88, 1980.

[4] T. Seike, and J. Nagai, “Electrochromism of 3d transition metal oxides,’’ Solar Ener. Mater. vol. 22, issue 2 - 3, pp. 107 - 117, 1991.

[5] A. M. B. Nasser, and M. S. Khil, “Synthesis and optical properties of two cobalt oxides (CoO and Co_3O_4) nanofibers produced by electrospinning process,’’ J. Phys. Chem. C, vol. 112, issue 32, pp. 12225 - 12233, 2008.

[6] F. Kadirgan, and M. Söhmen, “Development of black cobalt selective absorber on copper for solar collectors,’’ Turk. J. Chem., vol. 23, pp. 345 - 351, 1999.

[7] S. Pethkar, M. G. Takwale, and V. G. Bhide, “Cobalt oxide selective coatings for all glass evacuated collectors,’’ Sol. Ener. Mater. & Sol. Cells, vol. 31, issue 2, pp. 109 - 117, 1993.

[8] K. Chidambaram, L. K. Malhotra, and K. L. Chopra, “Spray-pyrolysed cobalt black as a high temperature selective absorber,’’ Thin Solid Films, vol. 87, issue 4, pp. 365 - 371, 1982.

[9] P. S. Patil, L. D. Kadam, and C. D. Lokhande, “Preparation and characterization of spray pyrolysed cobalt oxide thin films,” Thin Solid Films, vol. 272, issue 1, pp. 29 - 32, 1996.

[10] N. A. M. Barakat, B. Kim, H. Y. Kim, “Production of smooth and pure nickel metal nanofibers by the electrospinning technique: nanofibers possess splendid magnetic properties,’’ J. Phys. Chem. C, vol. 113, pp. 531 - 536, 2009.

[11] C. W. Tang, C. B. Wang, and S. H. Chien, "Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS,'' Thermochimica Acta, vol. 473, issue 1-2, pp. 68 -73, 2008.

[12] P. Nkeng, J. F. Koenig, J. L. Gautier, P. Chartier, and G. Poillerat, "Enhancement of surface areas of Co_3O_4 and $NiCo_2O_4$ electrocatalysts prepared by spray pyrolysis," J. Electroanalytical Chem. vol. 402, issue 1 - 2, pp. 81 - 89, 1996.

[13] K. L. Hung, C. H. Chi, C. T. Hsin, H. C. Shu, and B. W. Chen, Catal. Lett., "Synthesis, characterization and catalytic oxidation of carbon monoxide over cobalt oxide," vol. 88, issue 3 - 4, pp. 169 - 174, 2003.

[14] A. Gulino, and I. Fragala, Inorganica Chimica Acta, "Cobalt hexafluoroacetylacetonate polyether adducts for thin films of cobalt oxides," vol. 358, issue 15, pp. 4466 - 4472, 2005.

[15] T. S. Eriksson, A. Hjortsberg, and C. G. Granqvist, "Solar absorptance and thermal emittance of Al_2O_3 films on Al: A theoretical assessment," Solar Energy Mater. vol. 6, issue 2, pp. 191 - 199, 1982.

[16] P. Chrysicopoulou, D. Davazoglou, Chr. Trapalis, and G. Kordas, Thin Solid Films, "Optical properties of very thin (< 100 nm) sol–gel TiO_2 films," vol. 323, issue 1 - 2, pp. 188 - 193, 1998.

[17] F. Gu, C. Li, Y. J. Hu, and L. Zhang, "Synthesis and optical characterization of Co_3O_4 nanocrystals," J. Cryst. Growth, vol. 304, issue 2, pp. 369 - 373, 2007.