Optical Properties of DC Electrochemically Deposited Nanowired Co_3O_4 films

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Abstract

The preparation of nanowired Co_3O_4 films on copper (CU) substrates by using DC electrochemical deposition technique with $(CH_3COO)_2Co.4H_2O$ as precursor solutions in double distilled water and study of their optical properties are reported in this paper. The films are characterized by using XRD, SEM and UV-visible & FTIR spectroscopies. The characterization studies showed that the resultant films are impurity free, phase pure Co_3O_4 with cubic spinel symmetry and contain nanowires having diameter & length between 250 - 350 nm & 2 - 10 μm respectively. The resultant films showed the better values of absorptance (α) = 0.95, low emittance (ε) = 0.070 and selectivity = 13.57 as compared to reported data. These films are found to have good prospects for selective solar absorption coatings.

Keywords: Co_3O_4 films; Electrochemical deposition; Nanowires; Selective coating; Optical properties.

Introduction

Transition metal oxide semiconductor Co_3O_4 is used for many industrial applications. There are different methods for the deposition of Co_3O_4 films. The electrochemical deposition is very simple, cheap, versatile method for preparation and controlling the surface morphology of films as compared to other methods. The highest values of absorptance (a) in the range of 0.92 - 0.93 are reported in literature [1-2] for Co_3O_4 films. The film material can be tailored in terms of structure, grain size, absorptance, emittance and band gap energy. In view of this, the main objective of present work was to use the novel electrochemical deposition method for the preparation of the nanowired Co_3O_4 films with better optical properties as compared to the literature [1-2].

In this paper, preparation of nanowired Co_3O_4 films by using electrochemical deposition method reported. The resultant films were characterized by using XRD and SEM. The optical properties of resultant films were obtained by using FTIR spectroscopy and UV-visible spectroscopy studies.

Materials and Methods

The $(CH_3COO)_2Co.4H_2O$ (0.1 M) [CA] and H_3BO_3 (0.15 M) were dissolved one by one in 250 ml of double distilled water. This solution was filtered using Whatman 41 filter paper. The pH of solution was

maintained at ~ 4.5 by adding NaOH/ HCl in solution. This solution was used as deposition bath. The cobalt based thin films were deposited on thoroughly cleaned CU substrates by using a typical home-built DC electrochemical deposition system. The stainless steel (SS) substrates (area = 4 cm^2) were cleaned thoroughly by using the method reported in our earlier report [3]. The films were deposited at 7 different molar concentrations: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 M of CA in deposition bath by using the parameters: (a) cathode-anode distance = 2.5 cm, (b) pH of solution ~ 4.5, (c) current density = 10 mA/cm^2 and (d) deposition time = 12 min. The substrates deposited by the films were then washed gently in double distilled water by dip method. All the as-deposited films were heated at temperatures: 350 ^oC for 2 hr. The films prepared on CU substrates at 7 different molar concentrations: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 M of CA precursor were identified as EUA1, EUA2, EUA3, EUA4, EUA5, EUA6 and EUA7 respectively. The resultant films were characterized by using XRD [using X-ray diffractrometer (Bruker D8 Advance Machine, Germany with CuKα radiation λ = 1.5418 Å], SEM [JEOL JSM-6360-LA scanning electron microscope], UV-visible [JASCO Model: V670 spectrometer] spectroscopy and FTIR [JASCO make, Model: V6100A and FTIR-8400, Shimadzu, Japan] spectroscopy.

Results and Discussion

Fig. 1 gives the XRD patterns for EUA1 to EUA7 films. All the XRD patterns of different films are found to be similar to each other.

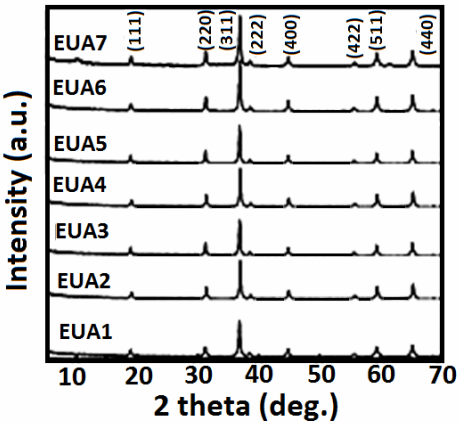

Fig. 1. (a) XRD patterns and (b) Raman spectra of resultant films

The peaks of all XRD patterns are perfectly matching with reflections due to the Co_3O_4 phase with cubic spinel symmetry given in JCPDS data file for Co_3O_4 [PDF-76-1802]. The peaks corresponding to other Co-oxide phases [4-7] are not observed in all the XRD patterns. The value of lattice parameter (a_o) obtained from the (400) reflection plane of XRD pattern of EUA5 films is found to be 8.052 Å. This value of 'a_o' is found to be very close the reported value of 8.084 Å for Co_3O_4 phase with cubic spinel symmetry [5-9]. All above observations indicate the formation of single phase Co_3O_4 with cubic spinel

symmetry in all the films deposited by using CA precursor on CU substrates and heated at 350 °C for 2 hr. This confirms material purity EUA1 to EUA7 films.

To understand the surface morphology of as-heated films, the scanning electron microscopy (SEM) study is undertaken. Fig. 2 gives the SEM images EUA1 to EUA7 films.

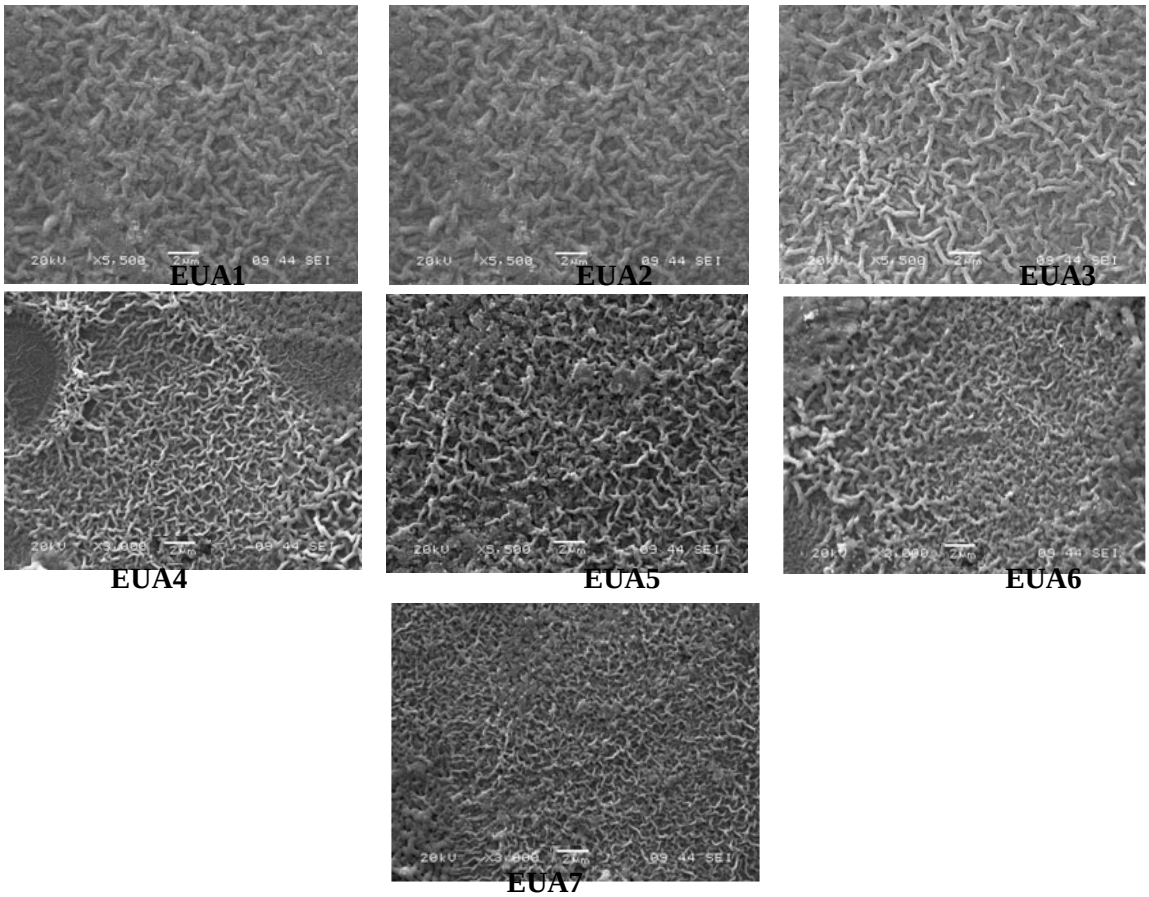

Fig. 2. SEM images for EUA1 to EUA7 films

The following observations are noted from SEM images: (i) surface of each film is covered with the mesh of interlinked wires, (ii) below the mesh of interlinked wires, surface is more or less smooth/flat, (iii) the interlinked wired mesh is attached firmly with base at different points with the insertion of ends of wires into the surface at that points, (iv) interlinked wires are more/less dense (i.e. rods like), (v) the diameters of 1-D interlinked wires are in the range of 250 - 350 nm, (vi) the lengths of 1-D interlinked wires are in the range of 2 - 10 μm and (vii) the densification at the surface of each film is moderate as per as the structure of 1-D interlinked wires is considered. However, qualitatively the densification is good below the interlinked wired mesh structure, because only 1 or 2 voids are seen at deep surface [8 - 15]. The qualitatively adhesion of all films to CU surfaces is found to be good. Fig. 3 (a) gives the FTIR

spectra for EUA1 to EUA7 films. The similar observations are noted for the films prepared for different molar concentration of CA precursor. The bands centered around 507 cm^{-1} and 584 cm^{-1} corresponding to the FCC CoO and hexagonal CoO(OH) respectively [5] are not observed in all the spectra. These bands are likely to be associated with Co ion in octahedral holes in an oxygen octahedral environment [16-17]. This confirm the purity of resultant films. The strong peaks characteristic of cubic spinel Co_3O_4 centered around 550 $cm^{-1}$and 665 cm^{-1} are observed in all the spectra. This indicates the formation Co_3O_4 phase in all the resultant films [18-19]. These 2 distinct bands originate from the stretching vibrations of the Co – O bonds [4, 20 -21]. The band around 550 cm^{-1} is associated with the OB_3 vibration in the spinel lattice [B denotes the Co^{3+} in an octahedral hole]. The band around 665 cm^{-1} is attributed to the ABO_3 vibration [A denotes the Co^{2+} in a tetrahedral hole] [22]. This clearly indicates the formation of single phase Co_3O_4 with cubic spinel symmetry in all the resultant films.

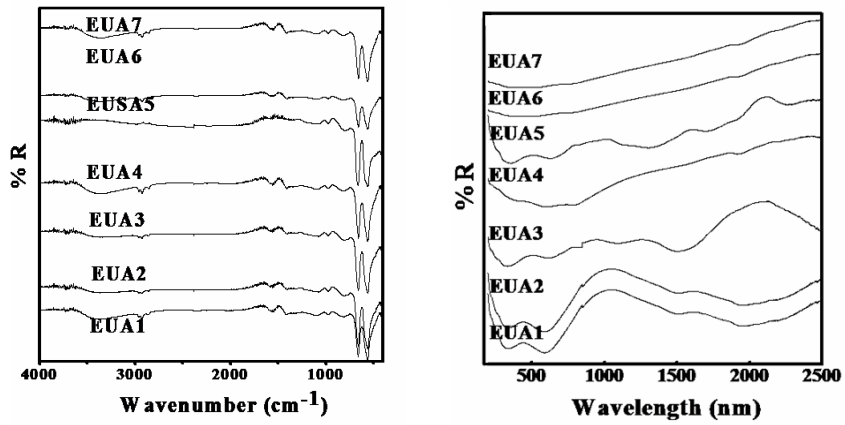

Fig. 3. (a) FTIR and (b) UV-Visible spectra for EUA1 to EUA7 films

Fig. 3 (b) gives the UV-Visible spectra for EUA1 to EUA7 films. The values of solar thermal absorptance (α) of these films are obtained from the UV-Visible reflection spectra.

The absorptance/absorptivity α(λ) is calculated by using the formula:

$$\alpha(T) = \frac{\int_{\lambda\min}^{\lambda\max} [1 - r(\lambda, T)] I(\lambda, T) d\lambda}{\int I(\lambda, T) d\lambda} \qquad (1)$$

Where, *I (λ, T)* = Intensity of black body radiation at wavelength λ and temperature T. Table - I gives the data for solar thermal absorptance (α) for EUA1 to EUA7 films. It is noted that the absorptance (α) is increasing with increasing the molar concentration of CA precursor upto 0.5 M. The highest value of absorptance (α) equal to 0.950 is for the EUA5 film prepared at 0.5 M concentration of CA precursor. This value of absorptance (α) is found to be higher than the reported data [23 - 29]. This indicates that the

optical properties of films depend on the molar concentration of precursor material in deposition bath. The FTIR spectra are used for the calculation of emittance/emissivity ε(λ) of these films. The values of emittance/ emissivity ε(T) of different films are calculated by using the formula:

$$\varepsilon(T) = \frac{\int_{\lambda\min}^{\lambda\max} [1 - r(\lambda,T)] I(\lambda,T) d\lambda}{\sigma T^4} \qquad (2)$$

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

Where, $\sigma = 5.6696 \times 10^{-8} wm^{-2}K^{-4}$ $C_1 = 3.7405 \times 10^{8} W\mu m^4 m^{-2}$ $C_2 = 1.43879 \times 10^{4} \mu mK$

Table - I gives the data for emittance (ε) for EUA1 to EUA7 films. The 'ε' is found to be increasing with increasing the molar concentration of CA precursor upto 0.2 M. Then 'ε' is decreasing with increasing the molar concentration of CA precursor upto 0.5 M. The values of 'ε' are found to be in the range of 0.070 - 0.100 for EUA1 to EUA7 films. The minimum values of 'ε' are found to be 0.070 for EUA5 (with α = 0.950) film. This value of 'ε' is found to be smaller than the reported data [23 - 29]. The optical data given in Fig. 3 (b) is analyzed by using the equation.

$$\alpha = \frac{\alpha_0}{h\nu}(h\nu - E_g)^n \qquad (3)$$

Where, α_o= constant, n = constant depending upon on the kind of optical transition (n = 1/2 and 2 for the direct and indirect transitions respectively). The resultant data is presented in fig. 4. Fig. 4 gives the variation of $(\alpha h\nu)^2$ with hν for EUA1 to EUA7 films.

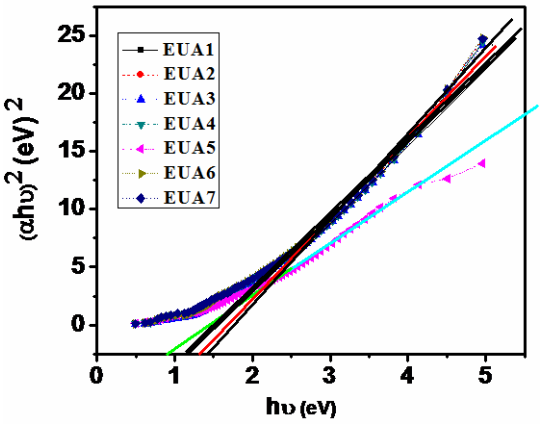

Fig. 4. Variation of $(\alpha h\nu)^2$ with hν for EUA1 to EUA7 films

The values of band gap energies (E_g) are obtained by extrapolation of the straight-line portions of the plots to zero absorption coefficients. The data for the band gap energy values is given in Table - I. These values of band gap energies are found to matching with the reported data [30 - 46] for Co_3O_4 phase.

Table – 1 Data For Absorptance (α), Emittance (ε) And Band Gap

Molar concentration of CA precursor	Film name	α	ε	E_g (eV)
0.1	EUA1	0.850	0.090	0.917
0.2	EUA2	0.880	0.100	1.165
0.3	EUA3	0.910	0.091	1.182
0.4	EUA4	0.920	0.080	1.301
0.5	EUA5	0.950	0.070	1.325
0.6	EUA6	0.930	0.075	1.359
0.7	EUA7	0.920	0.079	1.475

Conclusions

The DC electochemical deposition is simple, cheap and versatile processing route useful for the preparation of nanocrystalline spinel Co_3O_4 films. The Co_3O_4 films indicated the thickness dependent optical properties. The films with higher thickness showed the better values of α = 0.94, ε = 0.17 and selectivity = 5.529.

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