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STUDIES ON ELECTROCHEMICAL DEPOSITION AND CHARACTERIZATION OF Co_3O_4 FILMS

**P.N. Shelke^{1, 3}, Y.B. Kholam², K.R. Patil⁴, S.D. Gunjal³, S.R. Jadkar³,
M.G. Takwale³, K.C. Mohite³**

¹ Baburaoji Gholap College, New Sangvi, Pune 411 027, India
E-mail: pnschelke@gmail.com

² Arts, Commerce & Science College, Pirangut, 411 042, India

³ School of Energy Studies, Department of Physics, University of Pune,
Pune, 411 007, India

⁴ Center for Materials Characterization, National Chemical Laboratory,
Pune, 411 008, India

The Co_3O_4 films are prepared using two steps method. Initially, the films are electrochemically deposited on stainless steel and copper substrates from the solution containing CoSO_4 and H_3BO_3 at various molar concentrations (0.05, 0.09, 0.13, 0.17, 0.21, 0.25 and 0.28 M) of CoCl_2 in deposition bath. These as-deposited films are transformed into Co_3O_4 phase by heating them at 350 °C / 2 hr. These as-heated films are characterized by using X-ray diffraction, X-ray photoelectron spectroscopy, UV-Visible spectroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. From the characterization studies, the as-heated films are found to be containing single cubic spinel Co_3O_4 phase with high purity. The variation in molar concentration of CoCl_2 in electrochemical deposition bath showed the profound effect on optical properties of Co_3O_4 films. The better optical properties, (i) absorptance (α) = 0.945, emittance (ε) = 0.071 and (ii) absorptance (α) = 0.950, emittance (ε) = 0.070 are obtained for the Co_3O_4 films prepared on stainless steel and copper substrates respectively at 0.28 M concentration of CoCl_2 as compared to the data reported in literature. The strength and adhesion of as-heated films on both the substrates are found to be good for the molar concentrations of $\text{CoCl}_2 < 0.28$ M.

Keywords: Co_3O_4 FILMS, SELECTIVE COATING, ABSORPTANCE, EMITTANCE, ELECTROCHEMICAL DEPOSITION.

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1. INTRODUCTION

The films of cobalt oxide are very important in various applications like rechargeable batteries, electrochemical capacitors for high power devices in energy systems, electrochromic devices, solar absorber coatings, sensing, protective layers or pigment for glasses, ceramics etc. [1-5] due to their extremely interesting optical and/or electrical properties.

Different methods: electron beam evaporation, electrochemical deposition, chemical vapor deposition, chemical bath deposition, spray pyrolysis etc. are reported in literature for the preparation of cobalt oxide films [6-8]. The electrochemical deposition method is used successfully for a long time to (a)

prepare the semiconductor oxide films and (b) develop the solar collectors based on metallic oxide selective films deposited on copper substrates [9-12]. Room temperature (RT) processing, economically cheap and requirement of less instrumentation are the main characteristics of electrochemical deposition method. This method is useful for the production of thin homogeneous films. Because of having number of parameters like time, temperature, concentration of precursor, pH of solution, current density, type of electrolyte, cathode-anode distance etc. for the optimization, the electrochemical deposition method gives very good control over the composition, purity, morphology and thickness of the films.

Most of the research work regarding the electrochemical deposition of cobalt oxide films is related to (i) deposition of films on various substrates, (ii) physical characterization of films and (iii) study of optical properties of films. It is well known that the nature of substrate is also playing an important role in deciding the coating characteristics and optical properties of the films. In literature, the cobalt oxide (Co_3O_4) is proposed as a potential coating material for the selective surfaces [9, 13-17]. Sufficiently, high value of solar absorptance (α) = 0.93 and low value of thermal emittance (ε) = 0.09 are reported for the Co_3O_4 films deposited on nickel-coated glass substrates by using cobalt acetate as a cobalt precursor [11]. In another related work [14], the cobalt oxide films with optical properties: α = 0.93 and ε = 0.15 are prepared on stainless steel (SS) and copper (CU) substrates by using electrochemical deposition bath containing CoSO_4 and CoCl_2 solutions. However, the data related to the characterization of Co_3O_4 films are not given completely in the reported work [11, 14].

In view of this, the main aim of present work was to prepare the highly advantageous Co_3O_4 films on SS and CU substrates by using the novel electrochemical deposition method with better optical properties as compared to the data reported in literature [11, 14]. For this purpose, the cobalt based films are deposited on SS and CU substrates by varying the molar concentration of CoCl_2 precursor in deposition bath. All as-deposited films are heated at 350 °C / 2 hr. These as-prepared films are characterized by using different physical techniques: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The optical properties- reflectance (R), absorptance (α) and thermal emittance (ε) are measured for these as-prepared films.

2. EXPERIMENTAL

2.1 Cleaning of substrates

Initially, stainless steel (SS) and copper (CU) substrates (area of each substrate = 4 cm²) were cleaned thoroughly. The SS substrates were cleaned by dipping them in a solution containing 50 % HNO_3 and 10 % chromium at room temperature (RT) for 30 min. Then SS substrates were cleaned by dipping them in a solution containing 10 % H_2SO_4 at RT for 10 min to remove the effects of HNO_3 and chromium arised during the passivation treatment. These SS substrates were then rinsed with acetone to remove the effects of H_2SO_4 . The CU substrates were cleaned by dipping them in a solution containing 670 ml of orthophosphoric acid, 100 ml of H_2SO_4 and

270 ml of distilled water at RT for 30 min. The CU substrates were then cleaned with a solution of salt and lemon in double distilled water. Both, the SS and CU substrates were then subjected for cleaning with soap solution in double distilled water to remove the fingerprints if any. These substrates were again rinsed with acetone for 15 min. by dip method. Finally, the SS and CU substrates were cleaned with dilute detergent and warm water. After these treatments, the substrates were kept in acetone prior to the film deposition.

2.2 Preparation of films

The cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.98 M, 137 gm) and boric acid (H_3BO_3 , 0.30 M, 6.2 gm) were dissolved one by one in 500 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. It gives the deposition bath solution.

The cobalt based films were deposited on thoroughly cleaned stainless steel (SS) and copper (CU) substrates using electrochemical deposition method. Schematic diagram of a typical electrochemical deposition system is given in Fig. 1.

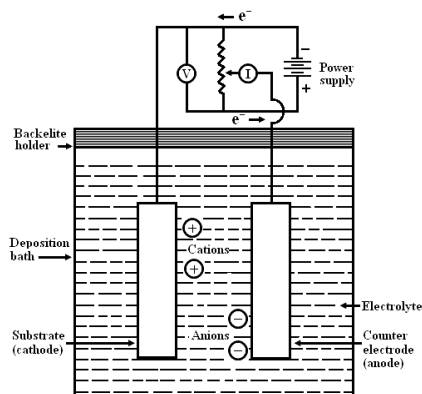


Fig. 1 – Schematic diagram of a typical electrochemical deposition system

The films were deposited at 7 different molar concentrations (0.05, 0.09, 0.13, 0.17, 0.21, 0.25 and 0.28 M) of cobalt chloride (CoCl_2) in deposition bath by using the parameters: (a) cathode-anode distance = 2 cm, (b) pH of solution ≈ 4.5 , (c) current density = 21 mA/cm^2 and (d) deposition time = 15 min. All as-deposited films were heated at $350^\circ\text{C} / 2 \text{ hr}$. The films prepared on SS substrates at 7 different molar concentrations - 0.05, 0.09, 0.13, 0.17, 0.21, 0.25 and 0.28 M of CoCl_2 are identified as SS1, SS2, SS3, SS4, SS5, SS6 and SS7 respectively. Similarly, the films prepared on CU substrates at 7 different molar concentrations - 0.05, 0.09, 0.13, 0.17, 0.21, 0.25 and 0.28 M of CoCl_2 are identified as CU1, CU2, CU3, CU4, CU5, CU6 and CU7 respectively. The thickness of each film was measured by using weight difference method. The values of thicknesses of the films deposited on SS and CU substrates were found to be in the range of $15 - 27 \mu\text{m}$.

2.3 Characterization of films

The films were characterized by using different physical techniques. The X-ray diffractometer (Bruker AXS, D8 Advance) was used for phase analysis of films. The impurity identification and phase analysis of films were done by using X-ray photoelectron spectroscopy. In X-ray photoelectron spectroscopy studies, a non-monochromatic MgK_{α} source at 1253.6 eV was used and pass energy of 50 eV was set at take off angle of 55° . The resolution of analyzer was approximately 1.6 eV. The error in photoelectron peak position was ± 0.2 eV. All binding energy (BE) values were charge corrected to C 1s $\equiv 285$ eV as an international standard. The optical properties- absorptance (α) and emittance (ϵ) of these films were obtained by using (a) UV-visible spectroscopy (JASCO, Corpn., Tokyo, Japan, UV-VIS-NIR Spectrophotometer, Model V-670 Sr. No.: A009761154) and (b) Fourier transform infrared spectroscopy (JASCO Corpn., Tokyo, Japan, FTIR Spectrometer, Model FTIR-4000, 6000 series) respectively. The scanning electron microscopy (SEM, Leica Stereoscan 440) was used for the morphological studies (particle size, shape, size distribution etc.) of films.

3. RESULTS AND DISCUSSION

3.1 UV- Visible spectroscopy studies

Fig. 2a and b give the UV-Visible spectra for cobalt oxide films – SS1 to SS7 and CU1 to CU7 respectively. The values of absorptance (α) for different films are obtained from the UV-Visible spectra.

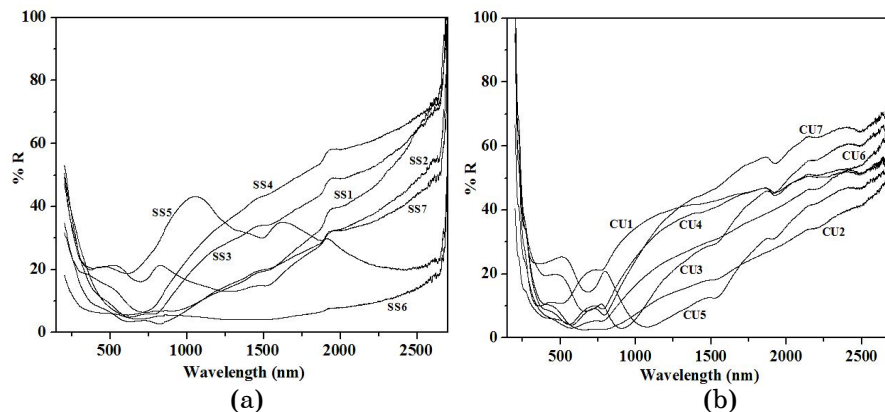


Fig. 2 – UV-Visible spectra for cobalt oxide films deposited on - SS (a) and CU substrates (b)

Fig. 3 gives the variation of absorptance (α) with molar concentration of $CoCl_2$ precursor in deposition bath during the deposition of films on stainless steel (SS) and copper (CU) substrates. In both the cases, it is noted that the absorptance (α) is increasing with increasing the molar concentration of $CoCl_2$. The highest values of absorptance (α) equal to 0.945 and 0.950 are found for the SS7 and CU7 films prepared at 0.28 M concentration of $CoCl_2$ respectively. These values of absorptance (α) are higher than the data reported

($\alpha = 0.92-0.93$) in literature [2, 11, 14]. Further, these values of absorptance (α) are obtained for the films prepared at lower molar concentration of H_3BO_3 (~ 0.30 M) as compared to the literature [2]. Furthermore, qualitatively, a poor adhesion to the substrate and high surface roughness are observed for the films prepared at higher molar concentration > 0.28 M of $CoCl_2$. Hence, the data for the films prepared at molar concentrations > 0.28 M of $CoCl_2$ are not recorded.

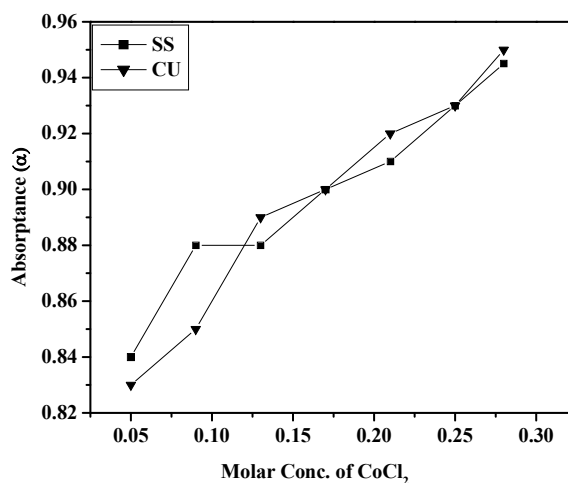


Fig. 3 – Variation of absorptance (α) with molar concentration of $CoCl_2$ precursor in deposition bath

3.2 Fourier transform infrared spectroscopy studies

Fig. 4 (a) and (b) give the Fourier transform infrared spectroscopy (FTIR) spectra for the films – SS1 to SS7 and CU1 to CU7 respectively. Similar observations are noted for the films prepared (i) on SS and CU substrates and (ii) for the different molar concentration of $CoCl_2$ precursor in deposition bath. No characteristic bands centered around 507 cm^{-1} and 584 cm^{-1} corresponding to the face centered cubic CoO and hexagonal $CoO(OH)$ respectively [18] are found in all the spectra. These single bands at 507 cm^{-1} and 584 cm^{-1} are likely to be associated with the cobalt ion in octahedral holes in an oxygen octahedral environment [19]. This clearly indicates the absence of impurities corresponding to face centered cubic CoO and hexagonal $CoO(OH)$ in the resultant 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 indicating thereby the formation Co_3O_4 phase in all the as-prepared films [20]. These two distinct bands originate from the stretching vibrations of the metal-oxygen bonds [21-23]. The band around 550 cm^{-1} is associated with the OB_3 vibration in the spinel lattice, where, B denotes the Co^{3+} in an octahedral hole. The band around 665 cm^{-1} is attributed to the ABO_3 vibration, where, A denotes the Co^{2+} in a tetrahedral hole. The values of emittance (ε) are obtained from the FTIR spectra for different films.

Fig. 5 gives the variation of emittance (ε) with respect to the molar concentration of CoCl_2 for the films- SS1 to SS7 and CU1 to CU7. Initially, in both the cases, ε is found to be increasing with increasing the molar concentration of CoCl_2 . For the molar concentration of $\text{CoCl}_2 > 0.13$ M, the ε is found to be decreasing continuously with increasing the molar concentration. The values of ε are found to be in the ranges of 0.071-0.110 and 0.070-0.107 for the different films - SS1 to SS7 and CU1 to CU7 respectively. The minimum values of ε are found to be 0.071 and 0.070 for the films- SS7 ($\alpha = 0.945$) and CU7 ($\alpha = 0.950$) respectively.

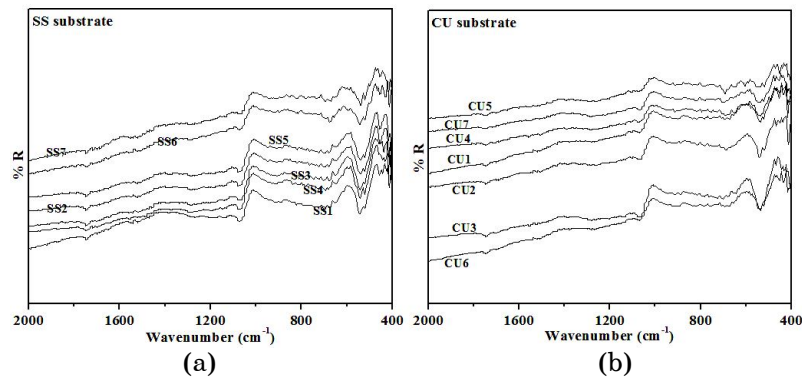


Fig. 4 – Fourier transform infrared spectroscopy (FTIR) spectra for the films deposited on – (a) SS and (b) CU substrates

These values of ε are found to be smaller than the data reported data in literature [2, 11, 14].

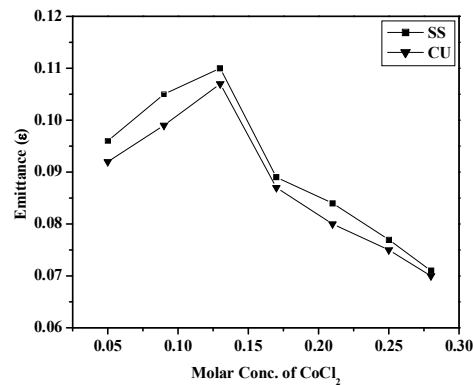


Fig. 5 – variation of emittance (ε) with respect to the molar concentration of CoCl_2 for the films- SS1 to SS7 and CU1 to CU7 deposited on SS and CU substrates

3.3 X-ray diffraction studies

The X-ray diffraction (XRD) pattern for a typical as-prepared film is shown in Fig. 6. The diffraction peaks corresponding to the Cobaltous oxide: CoO [JCPDS, PDF-71-1178] with face centered cubic symmetry and cobalt

oxyhydroxide: $\text{CoO}(\text{OH})$ [JCPDS, PDF-74-1057] with hexagonal symmetry are not observed in the diffraction pattern given in fig. 6 [22]. All the reflection lines match very well with the diffraction peaks given in JCPDS data file for Co_3O_4 [PDF-76-1802] with cubic spinel symmetry [18, 24, 25]. The lattice parameter calculated from the (400) reflection plane is found to be 8.059 Å, which is very close to the value reported (8.084 Å) for Co_3O_4 phase with cubic spinel symmetry [26, 27]. This clearly indicates the formation of single phase cubic spinel Co_3O_4 in the films prepared in present work.

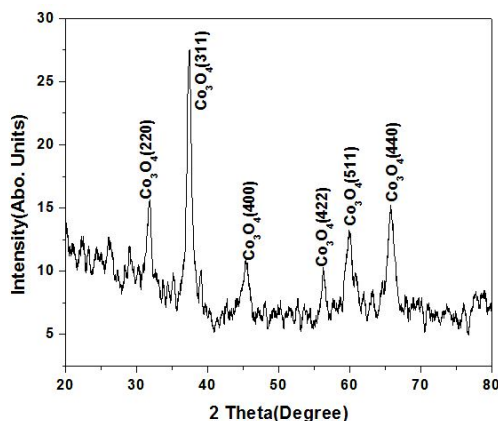


Fig. 6 – X-ray diffraction (XRD) pattern for a typical as-prepared film

3.4 X-ray photoelectron spectroscopy studies

The X-ray photoelectron spectroscopy (XPS) can be used for the elemental analysis, identification of valence state of element, stoichiometric findings and phase symmetry analysis in the films. Two films - SS7 and CU7 having good optical properties are taken for XPS studies.

The general survey scan XPS spectra (not shown here) of binding energy (BE) from 20 to 1000 eV for SS7 and CU7 films show two important observations. One, only the peaks corresponding to Co 2p, O 1s and C 1s are present in the given spectra. Secondly, the peaks corresponding to Cl, S etc., harmful to the electrical and/or physical properties of films are completely absent in the given spectra. This confirms the purity of films prepared in present work. Further, in order to identify the nature of cobalt oxide films, the Co 2p ($2p_{3/2}$ and $2p_{1/2}$) and O 1s core levels are recorded systematically at high resolution. The raw spectra of Co 2p and O 1s for SS7 and CU7 films are fitted using the XPSPEAK41 software program with Shirley + linear type background [28]. Fig. 7 a and b give the (i) slow scan high resolution XPS raw spectra, (ii) fitted curves and (iii) resultant curves for Co 2p core levels of SS7 and CU7 films respectively. Similarly, Fig. 8 a and b give the (i) slow scan high resolution XPS raw spectra, (ii) fitted curves and (iii) resultant curves for O 1s core levels of SS7 and CU7 films respectively.

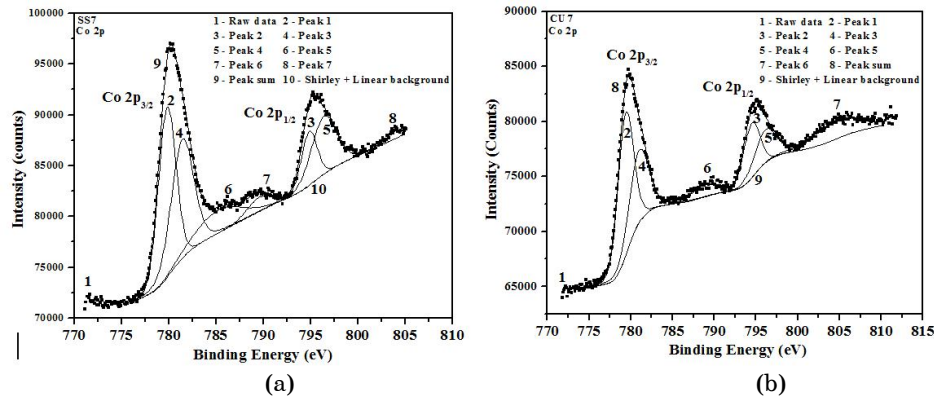


Fig. 7 – Slow scan high resolution XPS raw spectra, fitted curves and resultant curves for Co 2p core levels of SS7 (a) and CU7 films (b)

From Fig. 7 a and b two main observations are noted. One, we could fit the peaks corresponding to both Co^{2+} and Co^{3+} . This indicates the formation of single phase Co_3O_4 or Co_2O_3 with CoO , Co_2O_3 and CoOOH or the mixture of only CoO , Co_2O_3 and CoOOH in the SS7 and CU7 films. Secondly, in the present case, the shake-up satellite (SUS) structures, which are the fingerprints of electronic structure of spinel type oxide phases (i.e. Co_3O_4) [30] or CoO are clearly seen at the higher BE sides of main peaks maxima of Co 2p. This indicates the formation of Co_3O_4 and/or CoO as main phases in SS7 and CU7 films.

The data for:

- (i) core level peak positions – BE (eV) of Co $2p_{3/2}$ and Co $2p_{1/2}$ for both Co^{2+} (tetra.) and Co^{3+} (oct.), and BE (eV) of O 1s,
- (ii) shake-up satellites (SUS) towards the higher BE sides of main peaks maxima Co $2p_{3/2}$ & Co $2p_{1/2}$,
- (iii) Δ_1 (eV) = (BE of Co $2p_{1/2}$ – BE of Co $2p_{3/2}$) for both Co^{2+} (tetra.) and Co^{3+} (oct.) and
- (iv) Δ_2 (eV) = (BE of SUS – BE of Co $2p_{3/2}$) for both Co^{2+} (tetra.) and Co^{3+} (oct.) are obtained from the fitting of high resolution XPS scans and are summarized in Table 1.

Following observations are noted from the spectra given in Fig. 7 a and b. The values obtained for core level peak maxima of $2p_{3/2}$ Co^{3+} (oct.) are found to be 779.82 eV and 779.36 eV for SS7 and CU7 films respectively. These values are found to be very close to the reported values of 779.50 eV [30, 31, 32], 779.60 eV [33], 779.00 eV [34], and 780.10 eV [35] for Co_3O_4 phase. Further, the values obtained for core level peak maxima of $2p_{3/2}$ Co^{2+} (tetra.) are found to be 780.90 eV and 780.72 eV for SS7 and CU7 films respectively. These values are also found to be very close to the reported value of 780.70 eV [33] for Co_3O_4 phase. The values - 789.59 eV and 788.94 eV found for SUS for SS7 and CU7 films respectively are perfectly matching with the reported value 789.50 eV [33] of SUS for Co_3O_4 phase. In case of Co^{3+} (oct.), the values calculated for Δ_1 (eV) for SS7 and CU7 films are found to be 15.13 eV and 15.37 eV respectively. These values are found to be very close to reported values of 14.90 eV [33] and 15.1 eV [31, 35] for Co_3O_4 phase. Further, in case of Co^{2+} (tetra.), the values calculated for Δ_1

(eV) for SS7 and CU7 films are found to be 15.65 eV and 15.71 eV respectively. These values are also found to be very close to the reported value of 15.30 eV [33] for Co_3O_4 phase. More importantly, in case of Co^{3+} (oct.), the values obtained for Δ_2 (eV) for SS7 and CU7 films are found to be 9.77 eV and 9.58 eV respectively. These values of Δ_2 (eV) are found to be very close to the reported values of 9.0 eV [34] and 10.1 eV [31] for Co_3O_4 phase. In case of Co^{2+} (tetra.), the values obtained for Δ_2 (eV) for SS7 and CU7 films are found to be 8.69 eV and 8.22 eV respectively. These values of Δ_2 (eV) for Co^{2+} (tetra.) are also matching with the reported value of $\Delta_2 = 8.8$ eV [33] for Co_3O_4 phase. All these observations clearly indicate the formation of Co_3O_4 as a main phase of cobalt oxide in the SS7 and CU7 films.

To support the above conclusion, some more observations as given in the following discussion are noted from the spectra given in Fig. 7 a and b. The satellites observed in both spectra [Fig. 7 a and b] are due to the shake-up satellite (i.e. SUS) effects related to paramagnetic high spin Co^{2+} [30]. This clearly supports the conclusion of presence of Co^{2+} in the crystalline films of SS7 and CU7 as mentioned in above discussion.

From Fig. 7 a and b, following observations are noted.

- (i) Corresponding to CoO phase, very prominent SUS structures centered around 786 eV and 802 eV towards higher BE sides of main peaks maxima of $2p_{3/2}$ and $2p_{1/2}$ respectively are completely absent in both the spectra.
- (ii) These prominent SUS structures centered around 786 eV and 802 eV towards higher BE sides of main peaks maxima of $2p_{3/2}$ and $2p_{1/2}$ are arising at lower values of BE as compared to the corresponding SUS structures (a) reported for Co_3O_4 phase in literature [33] and (b) obtained in the present case [i.e. SUS- 789.59 eV and 803.89 eV for SS7 film and 788.94 eV and 804.72 eV CU7 film].
- (iii) The fast rising intensity structures arising due to SUS effect [as mentioned above in point (i)] and giving asymmetry to main peaks maxima of $2p_{3/2}$ and $2p_{1/2}$ at their higher BE sides are completely absent in both the spectra [Fig. 7 a and b and Table 1].
- (iv) The asymmetries in main peaks maxima of $2p_{3/2}$ and $2p_{1/2}$ at their lower BE sides arising due to the shoulders corresponding to Co^{2+} of CoO are not seen in these spectra.
- (v) The values obtained for Δ_2 (eV) for both Co^{2+} (tetra.) and Co^{3+} (oct.) [Table 1] are found to be very high as compared to the corresponding values of 5.2, 5.9 and 6.2 eV reported for CoO phase in the literature [31-33].

All these observations and related discussion given above clearly indicate the presence of Co^{2+} corresponding to the Co_3O_4 phase rather than CoO phase. Further, the large value of Δ_2 (eV) indicates the absence of CoO as an independent phase in the resultant crystalline films. Hence, the present films of SS7 and CU7 do not contain CoO as mixed phase or as an independent phase with main phase of Co_3O_4 . However, a very weak intensity SUS at BE = 785.23 eV is also observed [Fig. 7 a and Table 1] in the SS7 film. This might be due to the presence of extremely small amount of CoO in the main phase of Co_3O_4 of SS7 film.

Lastly, the values – BE of Co $2p_{3/2} = 782.4$ eV and $\Delta_1 = 16.0$ eV reported for CoOOH phase are found to be large as compared to the corresponding

values obtained in the present case [Fig. 7 and Table 1] for SS7 and CU7 films. Further, no shoulders corresponding to the BE = 782.4 eV towards the higher BE sides of main peaks maxima of Co 2p_{3/2} and Co 2p_{1/2} are found in both the spectra [Fig. 7 a and b]. This indicates the absence of CoOOH as a mixed phase in main phase of Co₃O₄. From all above observations and related discussion, it is clear that the SS7 and CU7 films contain only single cubic spinel Co₃O₄ phase. This is consistent with XRD and FTIR results.

As mentioned above, Fig. 8 a and b give the (i) slow scan high resolution XPS raw spectra, (ii) fitted curves and (iii) resultant curves for O 1s core level of SS7 and CU7 films respectively. Data obtained for the same are also presented in the Table 1.

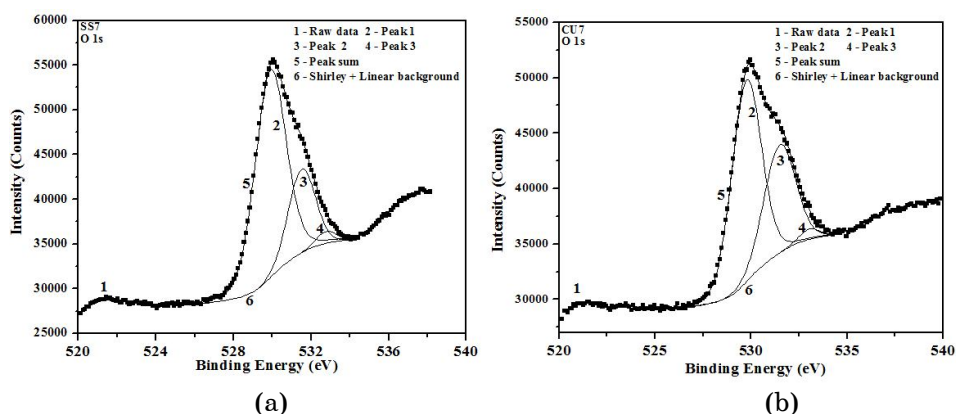


Fig. 8 – Slow scan high resolution XPS raw spectra, fitted curves and resultant curves for O 1s core level of (a) SS7 and (b) CU7 films

For each film, only three components are resulted during the fitting of each O 1s core level spectrum as reported in the literature [31]. The components obtained for SS7 film are found to be (i) 529.90 eV, (ii) 531.51 eV and (iii) 532.76 eV. Similarly, the components obtained for CU7 film are found to be (i) 529.76 eV, (ii) 531.49 eV and (iii) 533.00 eV. The 1st component around 529 eV is attributed to oxygen in the cobalt oxide compound [31]. The 2nd component around 531 eV is controversial in the literature [33]. This can be attributed to the presence of non-stoichiometric oxygen in the surface region or it can also include overlayer or incorporated oxygen atoms as well as OH⁻ adsorbed species [31]. The 3rd component around 533 eV with very low intensity can be attributed to the contamination of surface with the adsorbed water and/or carbonate [31] as well as with the adsorbed nitrates from electrochemical deposition solution.

Integer numbers in different brackets indicate the relevant peaks in Fig. 7 a and (b) and Fig. 8 a and b.

3.5 Scanning electron microscopy studies

To understand the surface morphology of as-prepared films, the scanning electron microscopy (SEM) study is undertaken. Fig. 9 (a) and (b) show the scanning electron microphotographs of SS7 (magnification = X12, 000) and CU7 (magnification = X18, 000) films respectively.

Table 1 – XPS BE values data for the films: SS7 & CU7

Sample	Co 2p				O 1s BE (eV)
	2p _{3/2} BE (eV)	2p _{1/2} BE (eV)	Δ_1 (eV)	Δ_2 (eV)	
SS7 film	779.82 Co ³⁺ (oct.)(1) 781.45 Co ²⁺ (tetra.)(3) 789.59 (SUS)(6) 785.23 (SUS)(5)	794.95 Co ³⁺ (oct.)(2) 796.55 Co ²⁺ (tetra.)(4) 803.89 (SUS)(7)	15.13 15.65 - -	9.77 8.69 - -	529.90 (73.72 %)(1) 531.51 (24.29 %)(2) 532.76 (1.99 %) (3) -
CU7 film	779.36 Co ³⁺ (oct.)(1) 781.23 Co ²⁺ (tetra.)(3) 788.94 (SUS)(5)	794.73 Co ³⁺ (oct.)(2) 796.43 Co ²⁺ (oct.)(4) 804.72 (SUS)(6)	15.37 15.71 -	9.58 8.22 -	529.76 (63.10 %)(1) 531.49 (34.89 %)(2) 533.00 (2.01 %) (3)
Co ₃ O ₄ [32]	779.60 Co ³⁺ (oct.) 780.70 Co ²⁺ (tetra.) 789.50 (SUS)	-	14.90 15.30	9.90	529.50 (53.00 %) 530.80 (47.00 %)
Co ₃ O ₄ [33]	779.00	-	-	9.00	529.90 531.40
Co ₃ O ₄ [29]	779.50 779.50 780.00	-	-	-	529.70 529.70 529.90
Co ₃ O ₄ [34]	780.10	-	15.10	-	-
CoO [29]	780.10 780.10 780.10	-	-	-	529.10
CoO [31]	780.50	-	16.00	5.20	529.60 (42.00 %) 530.48 (47.00 %)
CoO [32]	780.50	-	15.80	5.90	

The following observations are noted from both the microphotographs- (i) shape of each particle is diamond-like, (ii) each particle contains the different thin layers of diamond like structures, (iii) particle size distribution is nearly uniform, (iv) diamond-like particles are hard agglomerates or dense for SS7 film and (v) diamond-like particles are soft agglomerates for CU7 film. Further, both the microphotographs show number of voids at the surface of films indicating thereby the less densification and high surface roughness to each film at the surface. The average particle size is found to be ~ 1 μm for the diamond-like particles.

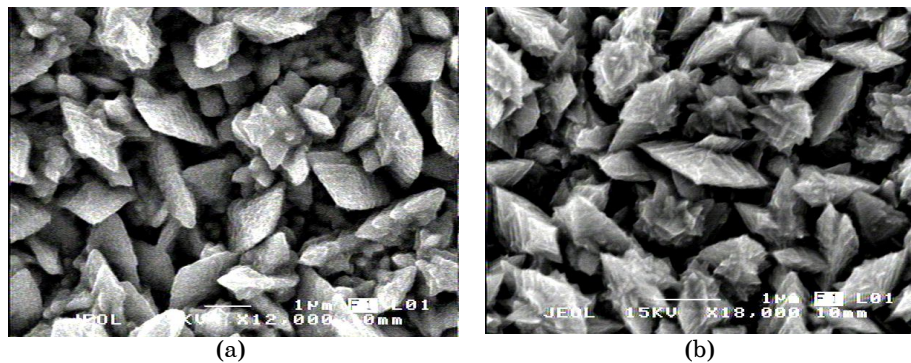


Fig. 9 – Show the scanning electron microphotographs of (a) SS7 and (b) CU7 films

4. CONCLUSION

The electrochemical deposition method is found to be cheap, easy for operation and room temperature processing of films. It needs less instrumentation as compared to the other physical and chemical methods. Method is very useful for the generation of highly pure and single phase Co_3O_4 films. The variation of molar concentration of CoCl_2 in electrochemical deposition bath showed profound effect on the optical properties of Co_3O_4 films. The variation of molar concentration of CoCl_2 is found to be useful for the generation of films on stainless steel and copper substrates having better optical properties: (i) $\alpha = 0.945$, $\varepsilon = 0.071$ and (ii) $\alpha = 0.950$, $\varepsilon = 0.070$ respectively as compared to the data reported in literature [11, 14]. Further, qualitatively, the strength and adhesion of films to the both substrates are found to be good for the films obtained at molar concentration of $\text{CoCl}_2 < 0.28$ M.

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