International Journal of Thin Films Science and Technology

http://dx.doi.org/10.18576/ijtfst/050302

The Effect of Solution pH on the Properties of Cobalt Oxide Thin Films Prepared by Nebulizer Spray Pyrolysis Technique

M. Manickam[1], V. Ponnuswamy[1,], C. Sankar[1], R. Suresh[1], R. Mariappan[2] and J. Chandrasekaran[1]*

[1] Thin film laboratory, Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore-641 020, Tamilnadu, India.

[2] Department of Physics, Adhiyamaan college of engineering, Hosur – 635 109, Tamilnadu, India.

Received: 4 Jul. 2016, Revised: 10 Aug. 2016, Accepted: 12 Aug. 2016.
Published online: 1 Sep. 2016.

Abstract: Single-phase cubic structured Cobalt oxide thin films were deposited on preheated glass substrates by Nebulizer Spray Pyrolysis (NSP) technique with different solution pH. The structural, optical, morphological and electrical properties were investigated. Cubic structured crystallites are detected by XRD pattern with preferential orientation along (220) direction. The transmittance of Co_3O_4 films increases with the increase of solution pH. The obtained bandgap values of Co_3O_4 films are found to be in the range 2.105 - 2.347 eV and 1.74 – 1.806 eV for higher and lower energy regions respectively. HRSEM images reveal the different morphologies like sphere-shaped particles, hexagonal shaped particles and coalescence of grains with solution pH. The maximum room temperature electrical conductivity (1.94×10^{-4} S/cm) is obtained at pH= 6. The electrical conductivity of the Co_3O_4 films increases with the solution pH upto pH = 6 then decreases for further increase of solution pH.

Keywords: X - Ray diffraction (XRD), Scanning Electron Microscopy (SEM), Electrical properties.

1. Introduction

Nebulizer spray pyrolysis (NSP) is one of the most promising methods employed to prepare metal oxide thin films like ZnO, SnO_2, MoO_3, and CeO_2 [1-4] etc. The NSP technique fulfils the required compatibility for the development of solar cell, P-N junction diode, heterojunction diodes and electrochemical electrodes etc. In recent years, supercapacitors are in demand for high energy storage system development. Supercapacitors are generally classified as Pseudocapacitors and Electric double layer capacitors (EDLC) and Pseudocapacitors have higher energy density than the EDLCs [5].

The NSP technique is the prominent method to prepare thin films and high-density pseudocapacitor electrodes. Low cost and non-toxic Co_3O_4 is a good alternate for RuO_2 to prepare higher energy density electrodes. The solution pH plays an important role in determining microstructural, morphological and electrical properties. The change in solution pH may change the property of the metal oxides. According to the earlier report, the solution pH plays a significant role in the structural, morphological, optical and electrical properties of the thin films prepared by sol-gel spin coating technique [6]. The change in property can improve the efficiency supercapacitors, gas sensor and fuel cells etc.

In the present investigation, Cobalt oxide thin films have been prepared by NSP technique with a variation of solution pH (pH= 4, 6 and 8). The solution pH values are controlled by adding HCl and NaOH solutions. Then the prepared films are characterized by XRD, UV-vis-NIR, HRSEM, EDAX, FT-IR and I-V characteristics.

2. Experimental details

2.1 Materials and film preparation

Cobalt oxide thin films are prepared by NSP technique by taking Cobalt chloride hexahydrate as a precursor material. The precursor solution is prepared by dissolving cobalt chloride hexahydrate in deionized water. The HCl and NaOH solutions are added drop wise to control the solution pH. To decrease the pH of the solution HCl is added to the precursor solution and the increase of solution pH is with NaOH solution. The prepared solution is stirred for 30 mins to get a clear solution. Then, 5 ml of the prepared solution is deposited onto the preheated glass substrate, which is maintained at 350°C. The carrier gas (air) pressure is maintained at 2.5 Kg/cm^2 and the solution is sprayed through a glass nozzle with 0.5 ml/min flow rate. When increasing solution pH by adding NaOH to the aqueous solution of cobalt chloride, cobalt hydroxide ($Co(OH)_2$) is formed and it

*Corresponding author E-mail: manickamphy011@gmail.com

is thermally decomposed into cobalt oxide. The deposited Co_3O_4 films with different solution pH are taken for characterization.

2.2 Characterization Techniques

The spray coated Co_3O_4 films are characterised by XRD, UV-Vis-NIR, HR-SEM, EDAX, FT-IR and electrical conductivity measurements. Structural analysis of Co_3O_4 films is carried out by using a XPERT-PRO Brucker AXS D8 advanced X-Ray Diffractometer with Cu Kα radiation (K= 0.15406 nm). The UV-Vis-NIR spectra of the sprayed film are analysed by JASCO spectrometer. Morphological and compositional analyses are carried out by High-Resolution Scanning Electron Microscope (HR-SEM) and Energy dispersive X-Ray analysis setup which is attached with HR-SEM (FEI quanta and FEG 200) respectively. Fourier transform Infra-Red spectra is taken by Brucker Alpha T spectrometer. I-V characteristics of the deposited films are studied by Keithley electrometer 6517 B. The analysed results are discussed and reported.

3. Result and Discussion

3.1 Structural analysis

Fig.1 shows the XRD pattern of Co_3O_4 thin films deposited at 350^{o}C with the solution prepared at different solution pH. The observed XRD peaks correspond to (111), (220), (311), (222) and (511) planes are located at 2θ= 18.59, 31.36, 36.46, 38.22 and 59.17 respectively. The XRD pattern shows that the prepared films are polycrystalline in nature with cubic structure having (220) preferential orientation. The obtained results are well matched with JCPDS data (card no. 89-1970).

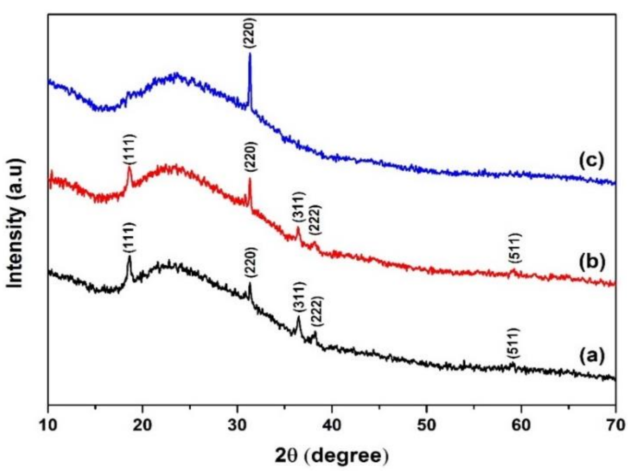

Fig. 1. X- ray diffraction patterns of Co_3O_4 thin films with solution pH a) pH= 4 b) pH= 6 c) pH= 8.

It is observed that the intensity of the peaks corresponds to (111), (311), (222) and (511) planes are decreased with an increase in solution pH. When the solution pH= 8, the intensity of all the peaks got diminished except for (220) plane. The (220) plane intensity increases with solution pH. The structural parameters like crystallite size, lattice constant, microstrain and dislocation density are calculated from the XRD analysis. The lattice constant of the prepared films is calculated from the following relation [7].

$$d_{(hkl)} = \frac{a}{\sqrt{(h^2+k^2+l^2)}} \qquad (1)$$

The lattice constant 'a' decreases with solution pH and is illustrated in fig. 2. An important parameter of thin films, crystallite size (D) is calculated from the well-known Scherrer formula [7].

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

where, K is the shape factor (0.94), λ is the wavelength of X-ray (0.15406 nm), β is the full width at the half-maximum and θ is the diffraction angle. The calculated crystallite size of prepared films is tabulated in table 1.

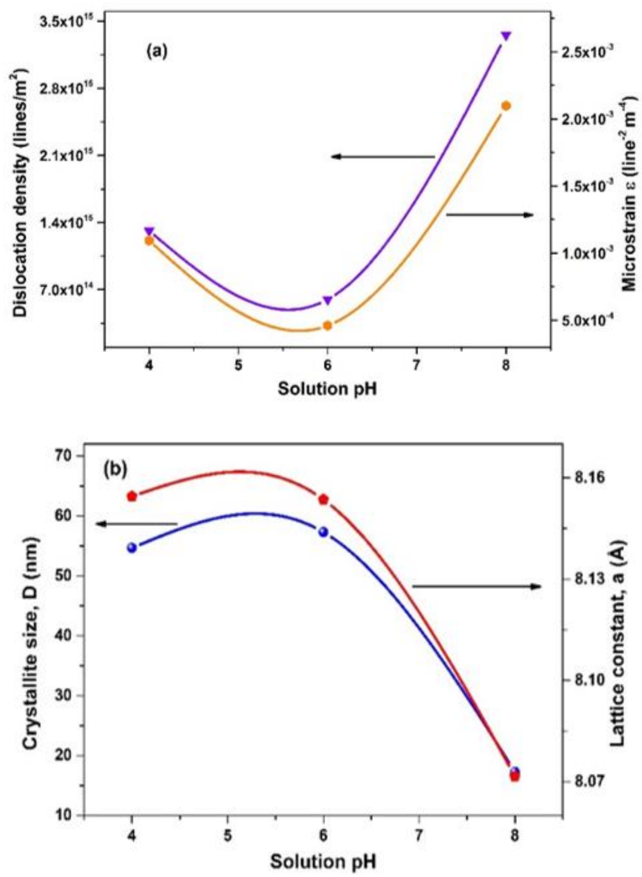

Fig. 2. (a) Microstrain and dislocation density (b) The variations of lattice constant and crystalline size, of Co_3O_4 films for different solution pH.

The crystallite size has a slight increase for solution pH=6 then decreases. The maximum crystallite size is found to be ~57 nm and the crystallite size for solution pH= 8 of the Co_3O_4 film is found to be ~17 nm. The microstrain and

Table. 1. Structural parameters of Co_3O_4 films with solution pH

Solution pH	2θ	FWHM	d-spacing(Å)	Lattice constant (Å)	Crystalline size D(nm)	Dislocation density δ (lines/m^2)	Microstrain ε (line^{-2}m^{-4})
4	18.5905	0.1623	4.77292	8.266939940	5.18039E-08	3.72628E+14	6.99E-04
	31.3695	0.4896	2.85166	8.065712495	1.76027E-08	3.22732E+15	2.06E-03
	36.4695	0.1246	2.46374	8.171301161	7.01129E-08	2.03425E+14	5.16E-04
	38.2282	0.4553	2.35434	8.155672997	1.92873E-08	2.68817E+15	1.88E-03
	59.1758	0.0833	1.56135	8.113012585	1.14545E-07	7.62162E+13	3.16E-04
6	18.6830	0.2000	4.74950	8.226375311	4.20444E-08	5.65696E+14	8.61E-04
	31.3444	0.4693	2.85389	8.072019887	1.8363E-08	2.9656E+15	1.97E-03
	36.4670	0.0900	2.46390	8.171831821	9.70668E-08	1.06135E+14	3.73E-04
	38.1010	0.4000	2.36191	8.181896246	2.19453E-08	2.07642E+15	1.65E-03
	59.1530	0.0890	1.56190	8.115870469	1.07197E-07	8.70233E+13	3.38E-04
8	31.3462	0.4992	2.85374	8.071595623	1.72632E-08	3.3555E+15	2.10E-03

dislocation density of the films are calculated from the following relation [8]

$$.\delta = \frac{1}{D^2} \quad (3)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (4)$$

The calculated values of microstrain and dislocation density are tabulated in table 1 and their variations are depicted in Fig.2. According to the result, the dislocation density and the microstrain have a decrease up to pH= 6 then show an increase for pH= 8. The decrease of dislocation density for pH= 6 shows the release of stress in the film and confirms the development of good crystallinity in the films.

3.2 Optical analysis

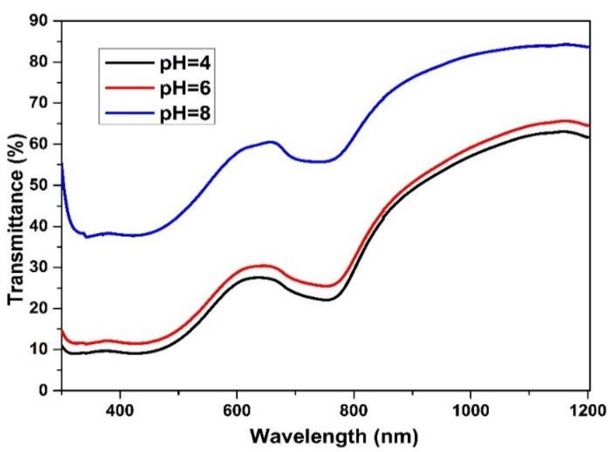

Fig. 3. Transmittance spectra of Co_3O_4 films with different solution pH.

The optical properties of the cobalt oxide thin films are analysed by UV-Vis-NIR spectrometer. The transmission spectra of Co_3O_4 films are illustrated in Fig. 3. It shows a maximum transmittance in the Infra-Red region.

For pH= 8 the film gives maximum transparency values about ~82% and ~62% in the IR and visible region respectively. The transmittance of Co_3O_4 films increases with the increase of solution pH which is due to the decrease of thickness and number of grains of the prepared films. The absorption coefficient of the prepared Co_3O_4 film is calculated from the following relation [9].

$$\alpha = \frac{\ln(1/T)}{t} \quad (5)$$

where, T is the transmittance and t is the thickness of the film. The bandgap energy is defined from the Tauc's relation [9]

$$(\alpha h\upsilon)^n = A(h\upsilon - E_g) \quad (6)$$

where, A is the constant, E_g is the bandgap energy and n is constant which is equal to 2, ½, 2/3, and 1/3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively. Fig. 4 shows the direct bandgap in the Co_3O_4 films obtained by extrapolating the linear plot of the $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) on the x-axis at $(\alpha h\upsilon)^2$=0. Two bandgap values are obtained from the two straight line portions which are due to the degeneracy of the valance band [10-14]. The obtained bandgap values of Co_3O_4 films are in the range 2.105 - 2.347 eV and 1.74 – 1.806 eV for higher and lower energy regions and are listed in table 2. The bandgap value of Co_3O_4 films decreases with the increase of solution pH due to the decrease of crystallite size in the films.

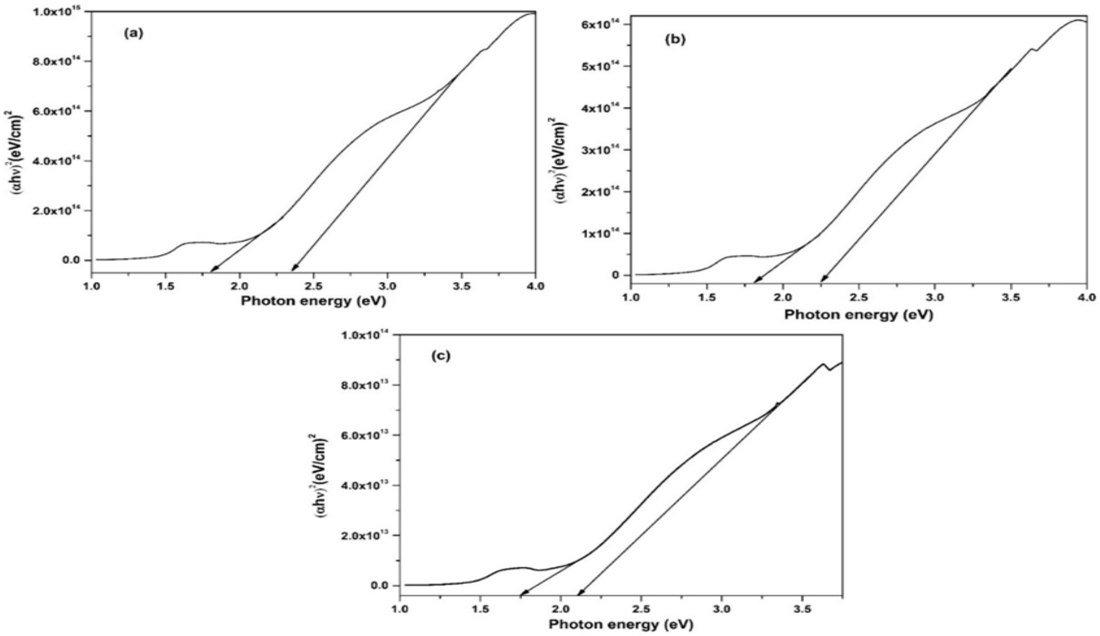

Fig.4. Plots of $(\alpha h\nu)^2$ against $h\nu$ of Co_3O_4 thin films with different solution pH, a) pH= 4 b) pH= 6 and c) pH= 8.

3.3 FT-IR analysis

Fig. 5 shows the FT-IR spectrum of the Co_3O_4 films recorded in the range 4000 to 500 cm^{-1} for different solution pH. The observed significant absorption peaks are 3462, 2917, 1262, 809, 688, 611 and 527 cm^{-1}. The intensity of the absorption band has a maximum for solution pH= 6. The absorption peak at 3462 cm^{-1} is attributed to the υ (O-H) mode of water molecule absorbed by the sample.

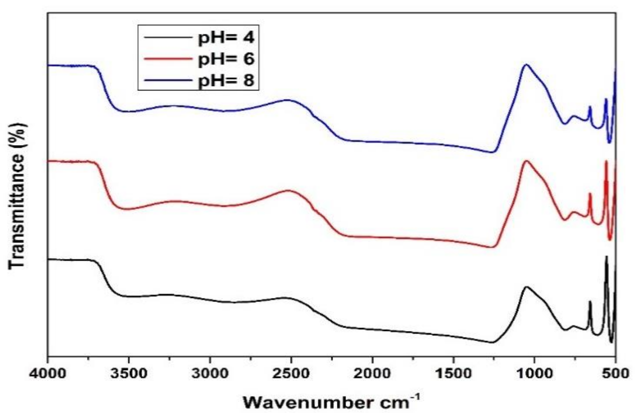

Fig. 5. FT-IR spectrum of Co_3O_4 films with different solution pH.

The low intensity band at 2917 cm^{-1} is assigned to υ(C-H) mode of organic moieties [4]. The two distinct bands at 688 and 611 cm^{-1} correspond to the optical vibration modes of Co_3O_4 [15].The absorption band at 527 cm^{-1} is assigned to stretching vibration mode of Co-O [16]. The presence of these optical vibration modes confirm the formation of Co_3O_4 in the films.

3.4 Morphological and Compositional analysis

Morphological analysis of Co_3O_4 films is carried out using High Resolution Scanning Electron Microscope. HRSEM images of Co_3O_4 thin films as a function of solution pH (pH= 4, 6 and 8) are shown in Fig. 6. At the solution pH= 4, the distribution of sphere shaped particles on the smooth surface is obtained. When pH is increased to 6, the sphere shaped particles changed into hexagonal shaped particles which are visualised at lower magnification. At higher solution pH, (pH= 8) the coalescence of grains is found in the film due to the decrease of grains Compositional analysis of Co_3O_4 thin films is analysed by Energy dispersive X-ray analysis and is shown in Fig.7. The atomic and weight percentage of the elements are listed in the insect table of the Fig. 7. The obtained spectrum confirms the presence of Co and O. The presence of impurities like Si and Ca peaks is due to the glass substrate. It is observed that the Co content decreases upto pH= 6 then increases and the O content is increased gradually with the solution pH which possess the morphological changes are evident from the HR-SEM images.

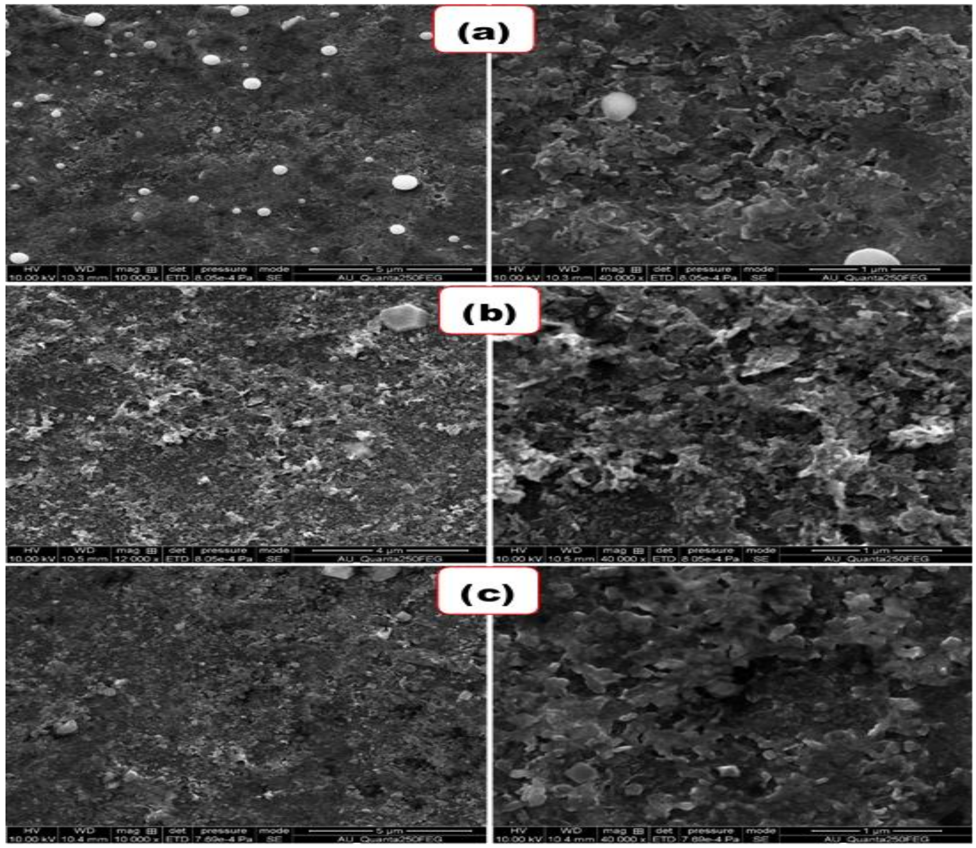

Fig. 6. HR-SEM images of Co_3O_4 thin films with different solution pH, a) pH= 4 b) pH= 6 and c) pH= 8.

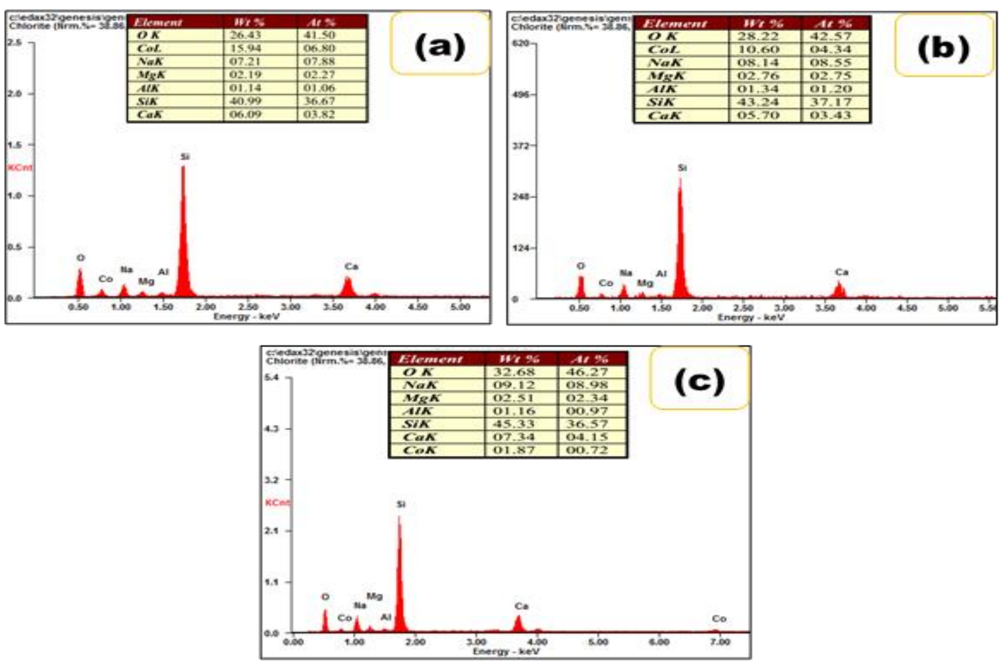

Fig. 7. EDAX spectrum of Co_3O_4 thin films with different solution pH.

3.5 Electrical properties

The I-V characteristics of Co_3O_4 films are carried out by Keithley electrometer 6517 B interfaced with a two probe setup. Fig. 8 shows the I-V characteristics of Co_3O_4 films for different solution pH. The applied potential ranges from 1 to 10 V and the corresponding current is measured as a function of temperature (RT – 120^{o}C) which indicates a linear (ohmic) behaviour of the films. The electrical conductivity of the prepared Co_3O_4 film is calculated from the following relation [9]

$$\sigma = \frac{1}{\rho} \quad (7)$$

$$\rho = \frac{RA}{l} \quad (8)$$

where, ρ is the resistivity, σ is the conductivity, R is the resistance, A is the cross sectional area of the film and l is the inter probe distance. Fig. 8 (d) shows the electrical conductivity of the Co_3O_4 film. The conductivity of the Co_3O_4 films increases with the solution pH upto pH= 6 due to higher crystallinity and increasing number of grains. When the solution pH increased to 8 the conductivity decreases due to the decrease of crystallite size and carrier density. These results are also evident from XRD analysis. The maximum room temperature electrical conductivity ($1.94\text{x}10^{-4}$ S/cm) is obtained at pH= 6. The electrical resistivity is in the order of 10^1 Ω.cm which is very low when compared with already reported results obtained with the sol-gel spin coating technique [6].

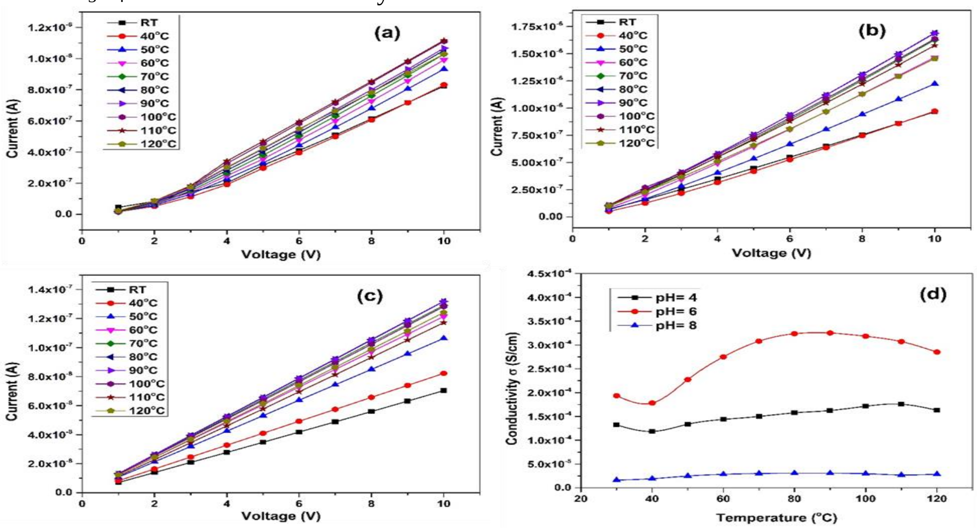

Fig. 8. I-V Characteristics of Co_3O_4 films with different solution pH, a) pH= 4 b) pH= 6 and c) pH= 8 d) Conductivity.

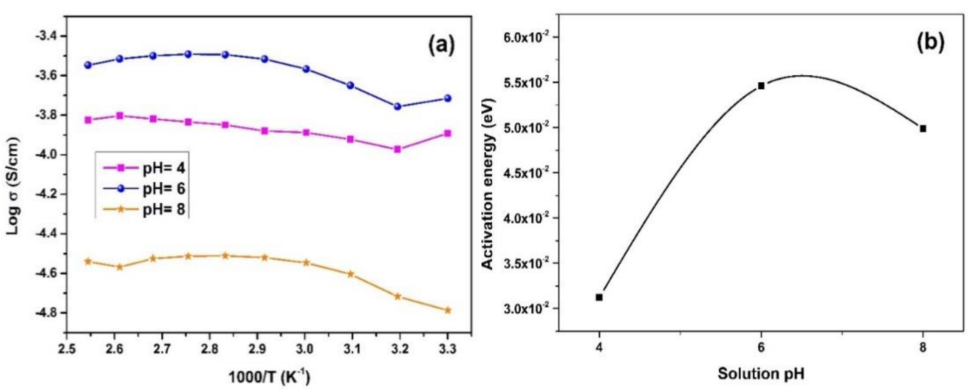

Fig. 9. a) Plot of Log σ vs. 1000/T b) activation energy for the Co_3O_4 films with different solution pH.

The activation energy of the Co_3O_4 films is calculated from the Arrhenius relation [17, 18].

$$\sigma = \sigma_o \exp\left[\frac{-E_a}{2K_BT}\right] \quad (9)$$

where, σ_o is the pre-exponential factor, K_B is the Boltzmann constant, E_a is the activation energy and T is the absolute temperature.

The activation energy is calculated from the slope of the Arrhenius plot, log σ vs 1000/T as shown in Fig. 9 (a) and variations in activation energy with solution pH is shown in Fig. 9 (b). The calculated activation energy is found to be in the range 0.031 to 0.054 eV. The solution pH changes the activation energy of the Co_3O_4 films due to the

Table. 2. Bandgap and activation energy of Co_3O_4 films.

Solution pH	Bandgap energy (eV)		Activation Energy (eV)
	E_{g1}	E_{g2}	
4	1.806	2.347	0.031212
6	1.79	2.25	0.054587
8	1.74	2.105	0.049888

corresponding changes in the film thickness and carrier density of the films.

4. Conclusion

Single phase cubic structured cobalt oxide thin films are prepared by NSP technique with different solution pH. The XRD pattern shows that the Co_3O_4 films are polycrystalline in nature with cubic structure having preferential orientation along (220) plane. The Co_3O_4 film prepared with solution pH=8 is found to have crystallites with an average size 17.26 nm. The crystallite size increases upto pH=6 then decreases for further increase. When pH= 8, the film has maximum transparency ~82% and ~62% in the IR and visible regions respectively. With the increase of solution pH, the transmittance increases whereas, the bandgap value decreases due to the decrease of film thickness and the crystallite size in the formed Co_3O_4 films. HRSEM images show the distribution of sphere-shaped particles on the smooth film surface. When pH= 6, the sphere-shaped particles are transformed into hexagonal shaped particles at lower magnification. At higher solution pH (pH= 8), the coalescence of grains is found in the film. The conductivity of the Co_3O_4 films increases with the solution pH upto 6 then decreased for further increase of solution pH. The film prepared at pH= 6 is found to have the maximum electrical conductivity 1.94×10^{-4} S/cm at room temperature. The calculated activation energy is found to be in the range 0.031 and 0.054 eV for the prepared films. The solution pH changes the activation energy of the Co_3O_4 films through its influence on film thickness and carrier density. From these investigations, it has been concluded that the solution pH has major role in the structural, optical, morphological and electrical properties of Co_3O_4 thin films.

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