Comparative NH_3 gas sensing characteristics of DC electrochemically deposited Co_3O_4 films by using different Co-based precursors

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Abstract: Herein, a comparative study of NH_3 gas sensing characteristics of DC electrochemically deposited Co_3O_4 films by using different Co-based precursors is reported. The Co_3O_4 films are deposited by using DC electrochemical deposition technique on thoroughly cleaned stainless steel (SS) and copper (CU) substrates. The Co_3O_4 films are deposited by using three water soluable Co-based precursors: $(CH_3COO)_2Co$, $Co(NO_3)_2$ and $CoCl_2$ with $CoSO_4$. All as-deposited Co-based films are annealed at 350 ºC for 2 hr. All resultant cobalt oxide films are characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The NH_3 gas sensing characteristcs of all resultant films are measured at room temperature by using static gas sensing system at different concentrations between 25 to 350 ppm of NH_3 gas. The structural studies using XRD showed that resultant films contain pure Co_3O_4 phase with cubic spinel symmetry. The topographical studies using SEM indicated different particle morphology like kite, spherical and interlinked nanowires of Co_3O_4 films genearted by using the $CoCl_2$ with $CoSO_4$, $Co(NO_3)_2$ and $(CH_3COO)_2Co$ precursors. The NH_3 gas sensing properties of resultant films showed lowest response time for the films generated by using $(CH_3COO)_2Co$ precursor. Further, recovery time is found to be lowest for the films generated by using $(CH_3COO)_2Co$ precursor on copper substrate. However, sensing studies of resultant films showed that the sensitivity factor (S.F.) is maximum for the films obtained by using the $CoCl_2$ with $CoSO_4$ precursor on both SS and CU substrates. For all resultant films, the response time (2 - 5 min.) is found to be higher than the recovery time (25 - 45 sec.). The repeatability and reproducibility in gas sensing characteritsic is noted for all films. The highest NH_3 sensing performance of $CoCl_2$ precursor derived Co_3O_4 films is linked with morphological charateristics of corresponding films.

Index Terms - Co_3O_4 film; DC Electrochemical deposition; NH_3 sensing; Sensitivity factor.

1. INTRODUCTION

The gas sensor is important domain for the field of research in material science. For human health and public safety, the sensor is playing very important at industrial sector and house household level [1- 4]. The NH_3 and LPG sensors are smaller in size, highly sensitive, cheap and easy in manufacturing [5-8]. The NH_3 and LPG sensors have number of applications in environmental, household and industrial problems. The low operating temperature, high stability, fast response, fast recovery, better selectivity, and most importantly high sensitivity are significant characteristics for the development of good sensors [9]. The Co_3O_4 is an important material for LPG and NH_3 sensing at low operating low temperature [10 - 12]. In view of this, the main objective of present research work was to study the NH_3 sensing response of Co_3O_4 films. Further, another important objective of present research work was to study the effect of morphology of particles of films on the gas sensing characteristics of Co_3O_4 films. Hence, for this purpose, cost effective, ease in operation and cheap DC electrochemical deposition technique was used for the preparation of the Co_3O_4 films. The resultant films were characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The NH_3 gas sensing properties were studied by using home-built static gas sensing characterization system. The results obtained related to the materials and NH_3 gas sensing characterization of DC electrochemically deposited Co_3O_4 films are presented in this communication.

2. EXPERIMENTAL DETAILS

2.1. Substrate cleaning

The stainless steel and copper substrates were used for the deposition of Co_3O_4 films. The 0.5 mm thick stainless steel (SS) substrates (area = 2 cm^2) were cleaned by dipping them for 30 min. in a solution having 50 % HNO_3 and 10 % chromium. Then substrates were cleaned by dipping them for 10 min. in a solution having 10 % H_2SO_4. After this substrates were rinsed with acetone to remove effects of prior cleaning. The 0.3 mm thick copper (CU) substrates (area = 2 cm^2) were cleaned by dipping them for 30 min. in a solution having 670 ml orthophosphoric acid, 100 ml H_2SO_4 and 270 ml double distilled water (DDW). Then substrates were cleaned by using a solution of salt and lemon in DDW. After this SS and CU substrates were cleaned by using soap solution in DDW. This is followed by rinsing of SS and CU substrates with acetone by dip method. Finally, both substrates were cleaned with dilute detergent and warm water. All the substrates were kept in acetone prior to the deposition of films.

2.2. Deposition of cobalt based films

On thoroughly cleanned SS and Cu substartes, the cobalt based films were prepared by using the DC electrochemical desposition technique and different water soluable Co-precursors.

(a) cobalt sulphate [$CoSO_4.7H_2O$] and cobalt chloride [$CoCl_2.4H_2O$] precursors

The $CoSO_4.7H_2O$ (0.98 M) and H_3BO_3 (0.30 M) were dissolved in 500 ml of DDW and solution was filtered using Whatman 41 filter paper. The pH of solution was kept at 4.5 by using NaOH / HCl in solution. It was the deposition bath. The films were deposited at 0.28 M concentration of cobalt chloride ($CoCl_2$) in deposition bath. The films were deposited by using the

parameters: cathode-anode distance = 2 cm, current density = 21 mA/cm^2 and deposition time = 15 min. The as-deposited films were washed gently in DDW by dip method. All the as-deposited films were heated at different 350 ^oC for 2 hr. The films prepared on SS and CU substrates were identified as ESC and EUC respectively.

(b) cobalt nitrate [$Co(NO_3)_2.6H_2O$] precursor

The $Co(NO_3)_2.6H_2O$ (0.1 M) and H_3BO_3 (0.12 M) were dissolved in 250 ml of DDW and solution was filtered using Whatman 41 filter paper. The pH of solution was maintained at 4.5 by using NaOH / HCl in solution. It was the deposition bath. The films were deposited at 0.5 M concentration of $Co(NO_3)_2.6H_2O$ in deposition bath. The films were deposited by using the parameters: cathode-anode distance = 2.5 cm, current density = 10 mA/cm^2 and deposition time = 8 min. The deposited films were washed gently in DDW by dip method. The as-deposited films were heated at 350 ^oC for 2 hr. The films prepared on SS and CU substrates were identified ESN and EUN respectively.

(c) Cobaltous acetate [$(CH_3COO)_2Co.4H_2O$] precursor

The $(CH_3COO)_2Co.4H_2O$ (0.1 M) and H_3BO_3 (0.15 M) were dissolved in 250 ml of DDW and solution is filtered using Whatman 41 filter paper. The pH of solution was kep at 4.5 by using NaOH/ HCl. It was deposition bath. The films were deposited at 0.7 M concentration of $(CH_3COO)_2Co.4H_2O$ in deposition bath. The films were deposited by using the parameters: cathode-anode distance = 2.5 cm, current density = 10 mA/cm^2 and deposition time = 12 min. The films were washed gently in DDW by dip method. The as-deposited films were heated at 350 ^oC for 2 hr. The films prepared on SS and CU substrates were identified as ESA and EUA respectively.

2.3. Characterization of as-prepared films

The as-prepared films were characterized by different physical techniques. The X-ray diffractometer (Bruker AXS, D8 Advanced) was used for structural analysis of films. The scanning electron microscope (SEM, JEOL JSM-6360-LA) was used for study of morphological features like particle size, shape and particle size distribution in resultant films. The NH_3 gas sensing characteristics: sensitivity factor (S.F.), response time, recovery time, repeatability and reproducibility of different as-prepared films were recorded by using home-built static gas sensing system at room temperature (RT).

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction studies

The formation of cobalt oxide in resultant films deposited on SS and CU substrates was studied by using X-ray diffraction patterns. Fig. 1 gives the X-ray diffraction patterns for the films deposited on SS and CU substartes by using the different cobalt precursors. In all XRD patterns, reflections corresponding to the face centered cubic, CoO [JCPDS, PDF-71-1178] and hexagonal CoO(OH) [JCPDS, PDF-74-1057] are not observed [1- 4]. All peaks observed in XRD patterns are found to be perfeclty matching with the reflections given for cubic spinel Co_3O_4 in JCPDS data file: PDF-76-1802. The values of lattice parameter are found to be very close to the reported value (8.084 Å) for cubic spinel Co_3O_4 phase [12]. This indicates that films deposited by using electrochemical deposition technique on SS and CU substrates contain pure single phase Co_3O_4 with cubic spinel symmtery when annealed at 350^o C for 2 hr.

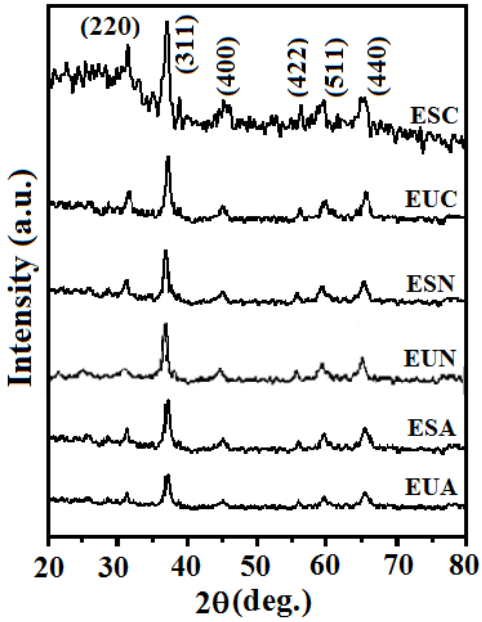

Fig. 1 X-ray diffraction patterns for the films deposited on SS and CU substartes by using the different cobalt precursors

3.2. Scanning electron microscopy

For morphological study of the resultant films, the scanning electron microscopy (SEM) study was undertaken. Fig. 2 shows the scanning electron microphotographs of the resultant films. The following observations are noted for ESC and EUC films. The shape of each particle is diamond-like and each particle contains the different thin layers of diamond like structures. The diamond-like particles are hard agglomerates or dense. The particle size distribution is nearly uniform. The numbers of voids are observed on the surface of films indicating thereby less densification and high surface roughness of each film. The average particle size is found to be ~ 1 µm. In case of films ESN and EUN, the spherical morphology is observed. The hard and soft agglomerates are observed in ESN and EUN films deposited on SS and CU substrates respectively. The size of the spherical agglomerates is in range of 1-3 µm.

The particle size distribution is almost uniform in these films. The voids also observed on the surface of these films showing thereby lower densification and high surface roughness in these films. Entirely different observations are found in case of ESA and EUA films. The surface of each film is found to be covered with the mesh of wires. The surface is flat at the bottom of the mesh of interlinked wires. These interlinked wires are found to be attached firmly to flat surface with the insertion of ends of wires into the surface at different points. The wires are dense and diameters of wire are found to be in range of 250 - 350 nm. Further, the lengths of the wire are found to be in the range of 2 - 10 μm. The mesh of interlinked wire structure is not very dense. However, the flat surface below the wired mesh structure is dense. Qualitatively, the adhesion of all the films to surface is noted to be very good.

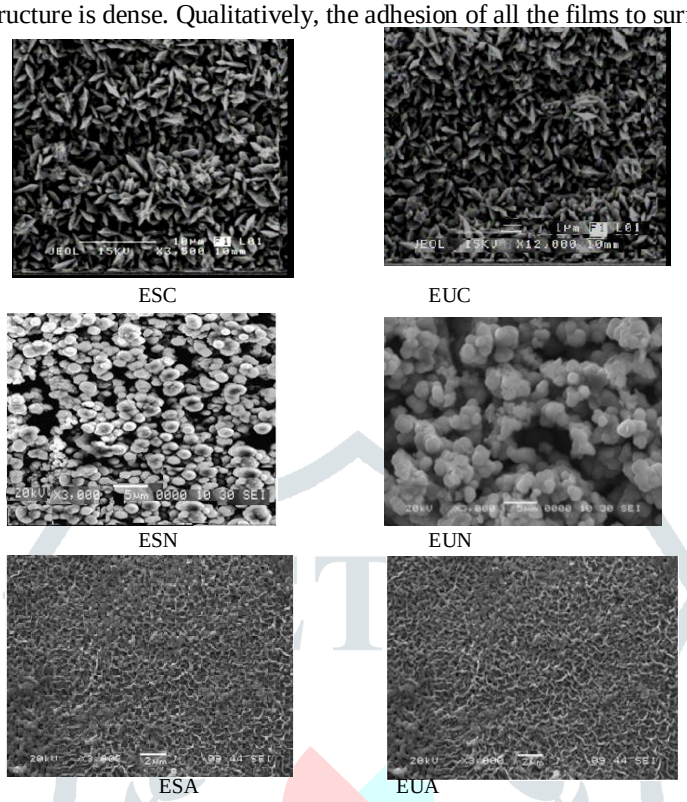

Fig. 2 SEM photographs for the films deposited on SS and CU substrates by using the different cobalt precursors

3.3. NH_3 sensing properties

Fig. 3 shows the variation of sensitivity factor (SF) with NH_3 gas concentration (in ppm) for the films deposited on SS and CU substrates by using the different cobalt precursors. For all films, initially, the SF is found to be increasing with increasing the NH_3 gas concentration to a certain value. After this, SF saturates to a constant value. The SF saturates above ~ 150 ppm concentration of NH_3 gas for the ESC, EUC, ESN and EUN films. However, for the ESA and EUA films the SF saturates above ~ 100 ppm concentration of NH_3 gas. The maximum values of SF are found to be 255 and 270 for the ESC7 and EUC7 films respectively. Further, the maximum values of SF are found to be 115 and 136 for the ESN5 and EUN5 films respectively. Furthermore, the maximum values of SF are found to be 155 and 145 for the ESA5 and EUA5 films respectively. The NH_3 gas sensing data properties: highest values of SF, response time and recovery time are summarized in Table 1.

The highest values of sensitivity factor are found to be decresing in the order (ESC, EUC), (ESA, EUA) and (ESN, EUN) as far as the cobalt precursor is concerned. Further, the SF is found to be higher for the films depositied on the CU substrate as compared to the films deposited on SS substrate. For all the films the response time is found to be much higher than the recovery time. The response time is of the order of few minute whereas the recovery time is of the order of second. This indicates the slow response of all the films in the presence of NH_3 gas. However, recovery of all sensor films is very fast on exposure of them to the air atmosphere. Further, response of ESA and EUA films to NH_3 gas sensing is faster as compared to the other films: ESC, EUC, ESN and EUN. Furthermore, the recovery of ESA and EUA films is also faster as compared to the other films: ESC, EUC, ESN and EUN. For all films, both response and recovery time are found to lower for the films deposited on CU substrates as compared to the films generated on the SS substrates.

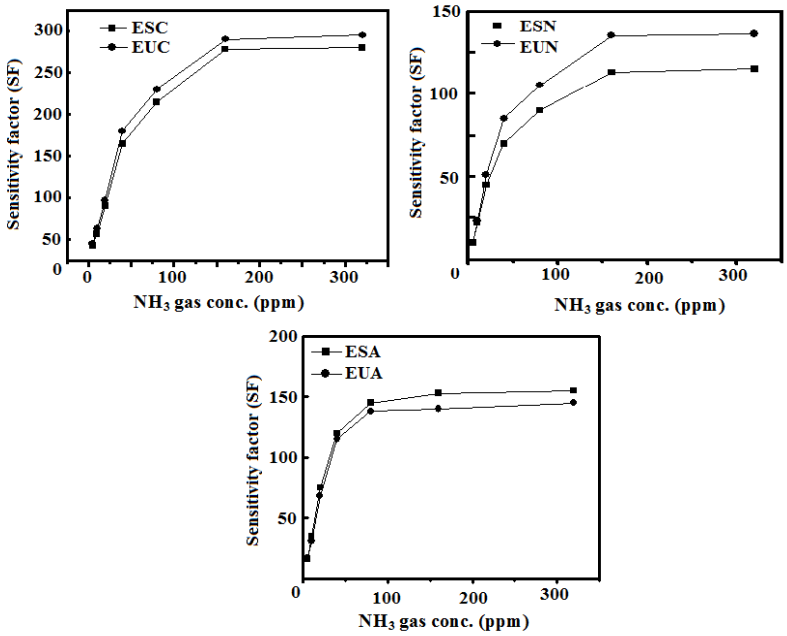

Fig. 3 Variation of sensitivity factor (SF) with NH_3 gas concentration (in ppm) for the films deposited on SS and CU substartes by using the different cobalt precursors

Table 1 NH_3 gas sensing data properties for the films deposited on SS and CU substrates by using the different cobalt precursors

Film name	Response time (min.)	Recovery time (sec.)	Sensitivity Factor (SF)
ESC	4.25	40	255
EUC	3.75	33	270
ESN	4.50	45	115
EUN	3.75	35	136
ESA	2.25	30	155
EUA	2.50	25	145

The repeatability of NH_3 gas sensing characteristics of all films was noted by measuring the gas sensing behavior of these films for number of the cycles. The NH_3 gas sensing behavior along-with the highest value of SF was found to be nearly constant in all the cycles for each film. This confirms the repeatability of NH_3 gas sensing characteristics of all films. Further, the gas sensing characteristics were also recorded for these films generated from the different batches of preparation. The almost similar gas sensing properties were found for these films generated from the different batches of preparation. This confirms the reproducibility of gas sensing properties of resultant films.

The gas sensing properties of the films deposited on SS and CU substartes by using the different cobalt precursors $CoCl_2$ with $CoSO_4$, $Co(NO_3)_2$ and $(CH_3COO)_2Co$ can be linked with the morphological features of the surface of these films. The highest NH_3 gas sensing performance obtained for ESC and EUC films can be linked with the special microstructure resulted in these films. In this case, the highest gas sensing properties might be due to diamond like structure of agglomerated Co_3O_4 particles. Further, each particle contains the different thin layers of diamond like structures with voids at surface of each films. These features give the high surface area leading to enhanced gas sensing characteristics. In case of ESA and EUA films, again special microstructure namely mesh of interlinked nanowires is obtained. However, the base of this mesh of interlinked nanowires is dense. This decreases the surface area leading to lower value of NH_3 gas sensing characteristics for ESA and EUA films as compared to ESC and EUC films. In case of ESN and EUN films, more voids are seen as compared to the ESC, EUC an ESA, EUA films. However, particles are hard and soft agglomerates. The particle size is higher in case of ESN and EUN films as compared to the ESC, EUC an ESA, EUA films. This has reduced further surface area of particles of ESN and EUN films. Due to this the NH_3 gas sensing properties particles of ESN and EUN films also further reduced.The lower response time in case of ESA and EUA films might be due to the interlinked nanowired structure present at the surface these films.

4. CONCLUSIONS

The DC electrochemical deposition is cheap-simple method for the preparation of films and needs less instrumentation. The Co_3O_4 films deposited by using this technique are uniformly thick with better adhesion to substrates. The NH_3 gas sensing properties of Co_3O_4 films deposited by using the different Co-precursors are found to be depending on the morphology of particles of films. Further, morphology of particles is found to be depending on the precursor used for the deposition of the films. For all films, response time is found to be much higher than the recovery time. The Co_3O_4 films deposited by using the $CoSO_4$ and $CoCl_2$ precursors are found to better for NH_3 sensing.

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