Spray pyrolysis deposited Co_3O_4 films for LPG and NH_3 sensing

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Abstract

The Co_3O_4 films were deposited on thoroughly cleaned stainless steel, copper and glass substrates by using spray pyrolysis deposition technique from solution of cobalt sulphate ($CoSO_4$:$7H_2O$) and cobalt chloride ($CoCl_2$:$4H_2O$) in 1:1 of mixture of water and methanol. As-deposited films were heated at 350 ^oC/2 hr. The resultant films were characterized by using X-ray diffraction, Raman spectroscopy, and scanning electron microscopy (SEM). The LPG and NH_3 gas sensing properties of these films were measured at room temperature (RT) by using static gas sensing system at different concentrations (~25 ppm to 350 ppm) of test gas. The XRD and Raman spectroscopy studies clearly indicated the formation of pure cubic spinel Co_3O_4 in all films. The LPG and NH_3 gas sensing properties of films showed the increase in sensitivity factor (S.F.) with gas concentrations and more sensitivity to LPG as compared to NH_3 gas. The maximum S.F. = 258 and 274 were found for NH_3 and LPG gases respectively for the films deposited on glass substrate. For all films, the response time (2- 4 min.) is found to be higher than the recovery time (30 - 45 sec.). For all films, the response and recovery time are found to be higher for LPG as compared to NH_3 gas. Further, repeatability - reproducibility in gas sensing properties was noted for all films.

Keywords: Co_3O_4 films; Spray Pyrolysis deposition; Gas sensing; LPG; NH_3; Sensitivity.

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1. Introduction

Nowadays, the detection of various types of gases is important topic in field of research. The sensors are playing an important role at household and industrial levels as far as public safety and human health are considered [1-4]. The LPG and NH_3 sensors are inexpensive, smaller in size, having high sensitivity and ease in fabrication [5-8]. They find the various applications related to industrial, household and environmental issues. The high sensitivity, high selectivity, quick response and recovery, low gas level detection, room temperature operating, high stability are few important characteristics for development of good sensors [9]. The p-type semiconducting Co_3O_4 could be a promising candidate for LPG and NH_3 sensors [10-12] at low operating low temperature. In this regards, the main aim of present research work was to study the LPG and NH_3 sensing response of Co_3O_4 films. For this intention, Co_3O_4 films are deposited by simple, and inexpensive spray pyrolysis technique. The spray pyrolysis technique doesn't require vacuum and high quality substrates or chemicals. The spray pyrolysed Co_3O_4 films are characterized and their LPG and NH_3 sensing behavior are recorded. The results obtained related to LPG-NH_3 sensing properties of spray pyrolysed Co_3O_4 films are presented in this paper.

2. Experimental

Substrate cleaning

Initially, The stainless steel (S) substrates (size = 2 cm x 2 cm, thickness = 0.5 mm) were cleaned by dipping them in a solution containing 50 % HNO_3 and 10 % chromium at room temperature (RT) for 30 min. Then substrates were cleaned by dipping them in a solution containing 10 % H_2SO_4 at RT for 10 minute to remove the effects of HNO_3 and chromium. These substrates were then rinsed with acetone to remove the effects of H_2SO_4. The copper substrates (size = 2 cm x 2 cm, thickness = 0.3 mm) were cleaned by dipping them in a solution containing 670 ml orthophosphoric acid, 100 ml H_2SO_4 and 270 ml doble distilled water (DDW) at RT for 30 min. Then substrates were cleaned with a solution of salt and lemon in DDW. Both substrates were further cleaned with soap solution in DDW to remove the fingerprints if any. These substrates were again rinsed with acetone by dip method for 15 min. Finally, both substrates were cleaned with dilute detergent and warm water. The glass (G) substrates (size = 7.5 cm x 2.5 cm, thickness = 1.2 mm) were boiled in chromic acid for 15 minutes and then washed with running tap water. Then substrates were washed with dilute detergent solution by dip method. Finally, the substrates were washed with DDW using ultrasonic cleaner for 30 min. After cleaning treatments, all the substrates were kept in acetone prior to the deposition of films.

Deposition of cobalt based films

The coablt based films were deposited on thoroughly cleaned above mentioned three substrates by using a typical home-built spray pyrolysis system. A 0.35 M spray solution of $CoSO_4.7H_2O$ and $CoCl_2$:$4H_2O$ was prepared in a 1:1 mixture of water + methanol. The films were prepared by using the parameters: (i) spray nozzle-substrate distance = 30 cm, (ii) spray nozzle diameter = 0.2 mm., (iii) flow rate for spray solution = 4 ml/min, (iv) flow rate for carrier gas = 9 lpm, (v) amount of spray solution = 60 ml and (vi) substrate temperature = 350 ^oC. The films were cooled naturally and removed from deposition chamber at room temperature (RT). The films deposited on stainless steel, copper and glass substrates were identified as S, C and G respectively.

Characterization of as-prepared films

The resultant 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 micro-Raman spectrometer (LABRAM HR – 800, Make: HORIBA JOBIN YVON, laser light with λ = 488 nm) was used for phase analysis of films. The scanning electron microscope (SEM, JEOL JSM-6360-LA) was used for the study of morphological features like particle size, shape and particle size distribution in resultant films. The LPG and NH_3 gas sensing characteristics: sensitivity factor (S.F.), response time, recovery time, repeatability and reproducibility of sensing characteristics of different as-prepared films were recorded by using home-built static gas sensing system at room temperature (RT).

3. Result and discussion

X-ray diffraction studies

To see the formation of cobalt oxide phases, the films deposited on stainless steel, copper and glass substrates were subjected for X-ray diffraction studies. Fig. (a) gives the X-ray diffraction patterns for the S, C and G films. From all XRD patterns, the following observations are noted. In all the XRD patterns, the diffraction peaks 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 the peaks match very well with the diffraction peaks reported for cubic spinel Co_3O_4 [JCPDS PDF-76-1802]. The values of

lattice parameter (a_0) calculated from the (400) reflection plane for the films: S, C and G are found to be 8.066 Å, 8.062 Å and 8.060 Å respectively. These values are found to be very close to the value reported (8.084 Å) for cubic spinel Co_3O_4 phase [12]. Thus the films deposited by using spray pyrolysis deposition technique on S, C and G substrates give the pure single cubic spinel phase Co_3O_4 films when heated at the temperature of 350 ^oC for 2 hrs.

Raman spectroscopy studies

Fig. 1 (b) gives the Raman spectra for S, C and G films. Similar observations are noted for all the spectra of S, C and G films. All Raman spectra show the four Raman-active modes ($A_{1g} + E_g + 2F_{2g}$). The peak with medium intensity located at 483 ± 2 cm^{-1} is attributable to the E_g phonon mode. The peaks with medium intensities located at 521 ± 2 cm^{-1} and 623 ± 2 cm^{-1} are ascribable to the F_{2g} phonon modes. The band located at 623 ± 2 cm^{-1} is attributed to the characteristics of the tetrahedral sites (CoO_4).

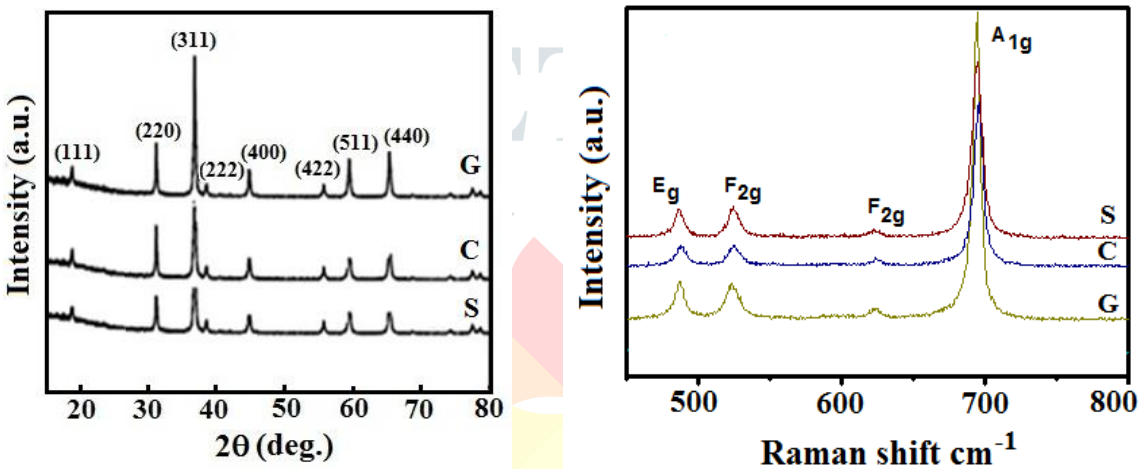

Fig. 1 (a) X-ray diffraction patterns and (b) Raman spectra for S, C and G films

The intense peak observed at 693 ± 2 cm^{-1} is due to the A_{1g} phonon mode in the $_Oh^7$ spectroscopic symmetry [13-18]. This band is attributed to the characteristics of the octahedral sites (CoO_6). Further, the Raman spectra of all films exhibit the close resemblance with Raman spectra reported for Co_3O_4 films [13-18]. The Raman spectroscopy studies on resultant films clearly indicate the formation of single cubic spinel Co_3O_4 phase in all the resultant films.

Scanning electron microscopy

Fig. 2 gives the scanning electron microphotographs for S, C and G films. The following observations are noted from all the SEM microphotographs: (i) film surface is covered with mesh of interlinked wires, (ii) below the interlinked wired mesh, surface is almost flat, (iii) the interlinked wired mesh is attached firmly to 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 distributions for diameters and lengths of interlinked wires are nearly uniform. (vi) the densification at the surface of each film is moderate as far as the structure of 1-D interlinked wires is considered. However, qualitatively, the densification below the interlinked wired mesh structure is good.

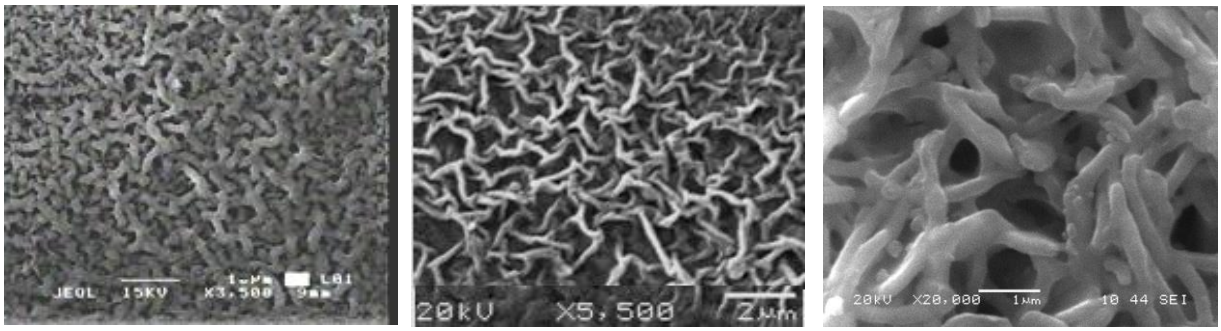

Fig. 2 Scanning electron microphotographs for S, C and G films

Gas sensing properties

The NH_3 and LPG gas sensing properties are obtained for S, C and G films. Fig. 3 gives variation of sensitivity factor (S.F.) with (a) NH_3 gas concentration (in ppm) and (b) LPG gas concentration (in ppm) for S, C and G films. In both the cases, S.F. is found to be increasing with increasing the gas concentration. After this, the S.F. saturates to different values for S, C and G films. The S.F. saturates at lower value of LPG gas concentration (~ 80 ppm) as compared to NH_3 gas concentration (~ 175 ppm) for the S, C and G films. This indicates that S, C and G films are more sensible to LPG gas as compared to the NH_3 gas. The highest values of S.F. are summarized in Table 1. In case of NH_3 gas sensing, the maximum values of S.F. are found to be 238, 246 and 258 for the S, C and G films respectively. Further, in case of LPG gas sensing, the maximum values of S.F. are found to be 239, 251 and 274 for the S, C and G films respectively. This further indicates that all three films are more sensible for LPG gas as compared to for NH_3 gas. For sensing repeatability studies, the NH_3 and LPG gas sensing behavior are recorded for S, C and G films for 3 cycles. The sensing repeatability curves are recorded at 200 ppm and 90 ppm concentrations of NH_3 gas and LPG gas respectively. These concentrations of NH_3 and LPG gases are selected because at these concentrations the maximum values of S.F. are obtained. Fig. 4 (a) and (b) give variation of film resistance with time for 3 cycles for the S, C and G films at 200 ppm of NH_3 gas and 90 ppm of LPG gas respectively. Both figs. 4 (a) and (b) clearly indicate the repeatability in gas sensing behavior of S, C and G films for both NH_3 and LPG gases. Similar trends in variation of resistance with time in the presence of given gas are noted for 3 cycles for all 3 films. This confirms the repeatability of gas sensing behavior of these films. The response and recovery times are noted for S, C and G films for NH_3 and LPG gases. The data for this is given in the Table 1. For all 3 films, the values of response time are found to be smaller for NH_3 gas than for LPG gas.

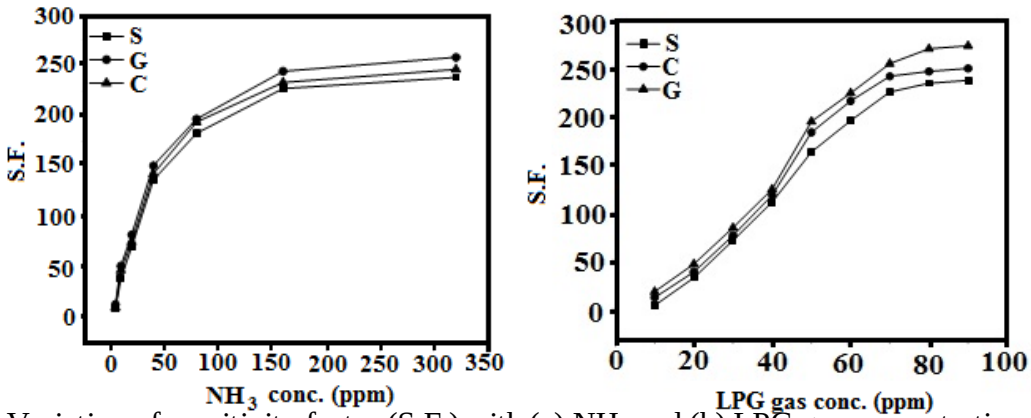

Fig. 3 Variation of sensitivity factor (S.F.) with (a) NH_3 and (b) LPG gas concentration (in ppm) for the S, C and G films.

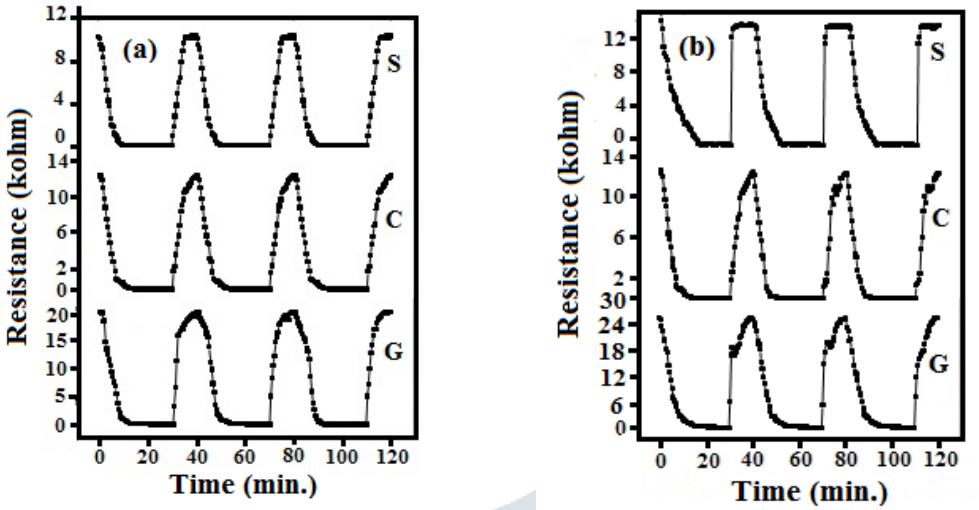

Fig. 4 Variation of resistance with time for 3 cycles for the S, C and G films at (a) 200 ppm of NH_3 gas and (b) 90 ppm of LPG gas.

Table 1 Data for response time, recovery time and sensitivity factor (S.F.)

Film name	Test gas	Response time (min.)	Recovery time (sec.)	Sensitivity factor (S.F.)
S	NH_3	3.50	40	238
C	NH_3	3.25	30	246
G	NH_3	2.75	30	258
S	LPG	4.00	45	239
C	LPG	3.50	40	251
G	LPG	3.00	40	274

Conclusions

The spray pyrolysis deposition technique is cheap, simple and needs less instrumentation. The Co_3O_4 films are more sensible to LPG gas and LPG-NH_3 sensing behavior of films is highly reproducible. For all films, response time is much higher than the recovery time. The LPG-NH_3 sensing behavior of spray pyrolysed Co_3O_4 films are found to be better for sensing application.

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