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

P. N. Shelke[a,*], Y. B. Khollam[b], M. T. Sarode[c]

[a]Department of Physics, Anantrao Pawar College, Pirangut, Pune 412 115, India.

[b]Department of Physics, Baburaoji Gholap College, Sangvi, Pune 411 027, India.

[c]Department of Physics, Mahatma Phule Mahavidyalya, Pimpri, Pune 411 017, India.

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 °C 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