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Gas sensing properties of Co surface modified $SmFeO_3$ thick film

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Abstract

The surfaces of p-type $SmFeO_3$ thick film were modified by simple dipping method. $SmFeO_3$ films prepared onto glass substrate were inserted into a cobalt chloride solution for 5 min. These films were fired in muffle furnace and their FE-SEM and EDX micrographs were recorded. The films were porous in nature and well dispersion of cobalt particles on the surface of $SmFeO_3$ film was observed. Gas sensing performance of as-prepared Co-$SmFeO_3$ film was analyzed in presence of ammonia, ethanol, hydrogen, LPG, carbon dioxide and chlorine. The observations showed that the film was selective to ammonia and exhibited better gas response as compared to $SmFeO_3$ film. Maximum gas response to 50 ppm ammonia at 200 ^{0}C was 6.39 which was three times more than that of $SmFeO_3$ film. The effect of Co surface modification on microstructure and ammonia gas sensing properties $SmFeO_3$ film was discussed.

Keywords: Surface modification, Gas Response, selectivity, Chemisorption, Reducing gas.

1. Introduction

Need of environmental monitoring has made considerable amount of research in solid state gas sensors based on semiconductor metal oxides. ZnO, TiO_2, SnO_2 and their composites are well known materials for solid state gas sensors [1-3]. Some ABO_3- type perovskites such as $SmFeO_3$ also presented good gas sensing characteristics [4]. P-type $SmFeO_3$ has been investigated repeatedly by my researchers in the fabrication of sensors for the monitoring of oxidizing gases such as ozone [5]. But under reducing condition, phase separation and low electrical conductivity was observed for P-type $SmFeO_3$ [6]. The electrical conductivity can be increased by creating more oxygen vacancies on the surface of material. Addition of oxidizing or reducing elements to $SmFeO_3$ is better approach for increasing the number of oxygen vacancies at its surface. This can be achieved either by doping method or dipping method. Co, Ce and Ni dopants were investigated for the modification of $SmFeO_3$ [7-8]. Cobalt is reducible element addition of which to pure $SmFeO_3$ can induce more oxygen vacancies. In cobalt doped $SmFeO_3$, each Co^{2+} ion delivers one electron and therefore Co misfit act as oxygen vacancy [9].R. C. Michel reported synthesis and characterization of $SmCoO_3$ for enhanced gas sensing. Since Co-O bond is weaker than Fe-O bond, problem of chemical stability can arise for reducing gases. Therefore addition of controlled amount of Co to pristine $SmFeO_3$ is essential.

In our previous work, nanocrystalline $SmFeO_3$ powder was prepared by sol-gel method and SmFeO3 thick film was fabricated onto glass substrate by screen printing method [10]. In present investigation, as prepared $SmFeO_3$ film was surface modified with cobalt and the corresponding gas sensing properties were studied.

2. Experimental

As reported in our earlier work, nanocrystalline $SmFeO_3$ powder was synthesized by sol-gel method and $SmFeO_3$ films were formed onto the glass substrate by screen printing technique [10]. 0.1 M aqueous cobalt chloride solution was prepared by using $CoCl_2 6H_2O$ and distilled water. To this solution, as prepared $SmFeO_3$ film was dipped for 5 min. Finally the film was fired for 30 min at 550 ^{0}C before applying for further investigations.

The microstructure of Co-$SmFeO_3$ film was observed by FE-SEM technique. The wt % of Sm, Fe, O and Co present on the film was measured in EDX spectra. Gas sensing performance of as prepared Co-$SmFeO_3$ film was tested in static gas sensing set-up. Target gases employed in the experiment were ammonia, ethanol, hydrogen, LPG, carbon dioxide and chlorine.

3. Results and Discussion

3.1. XRD, morphological and elemental analysis:

The recorded XRD spectra of as prepared nanocrystalline $SmFeO_3$ powder was explained in previous publication conforming the formation of pure polycrystalline $SmFeO_3$ with average crystallite size 50 nm [10].

FE-SEM micrographs and EDX spectra of Co-$SmFeO_3$ film was presented in Fig. 1 and Fig. 2 respectively.

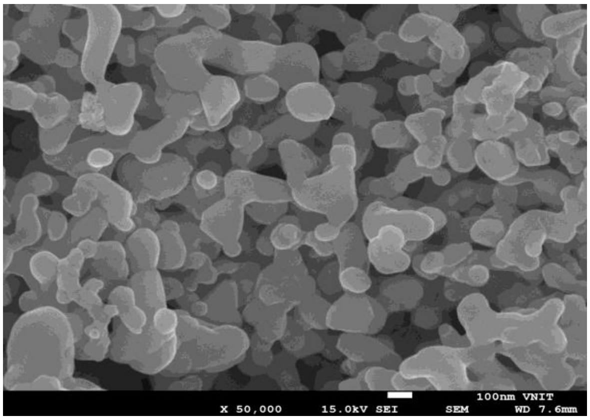

Fig. 1: FE-SEM of Co-$SmFeO_3$ film

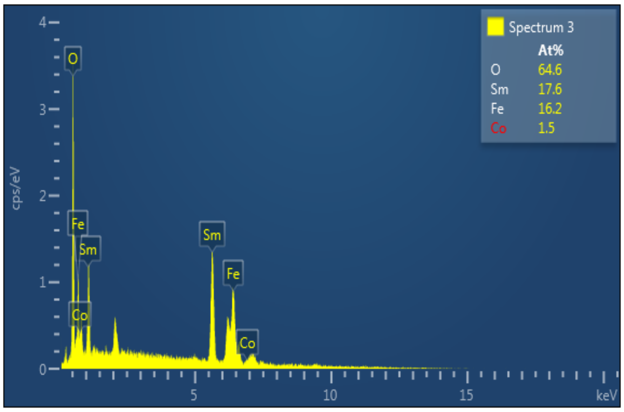

Fig. 2: EDX image of Co-$SmFeO_3$ film

FE-SEM micrograph seems to be consists of large number of grains having size in the range 47 nm to 80 nm. Particles appear irregular in shape and the agglomeration of particles was also observed at some places. Co particles might be distributed around the larger grains. Porosity observed in Co-$SmFeO_3$ film favours adsorption and desorption processes. EDX spectra of Co-$SmFeO_3$ film confirmed the incorporation of Co on the surface of $SmFeO_3$ film. Co has occupied Sm or Fe sites in $SmFeO_3$ perovskite structure.

3.2 Gas sensing properties:

Performance of gas sensor is generally determined from its gas response, optimal operating temperature, selectivity and stability. For p-type SMO, gas response is expressed as (R_g/R_a) where R_g and R_a represents resistance of semiconducting material in target gas and in air respectively [11]. In our previous work, $SmFeO_3$ film was selective to ammonia gas but the gas response to 50 ppm ammonia gas at 200 ^{0}C was only 2.07. In present investigation, Co-$SmFeO_3$ film was also selective to ammonia gas but this time the response was 6.39 which is three times larger than the response of pure $SmFeO_3$ film although the optimal operating temperature was same.

To study temperature dependence of gas response, the responses of Co-$SmFeO_3$ film to 50 ppm ammonia were calculated at different operating temperatures ranging from 30 ^{0}C to 400 ^{0}C and presented in Fig.3.

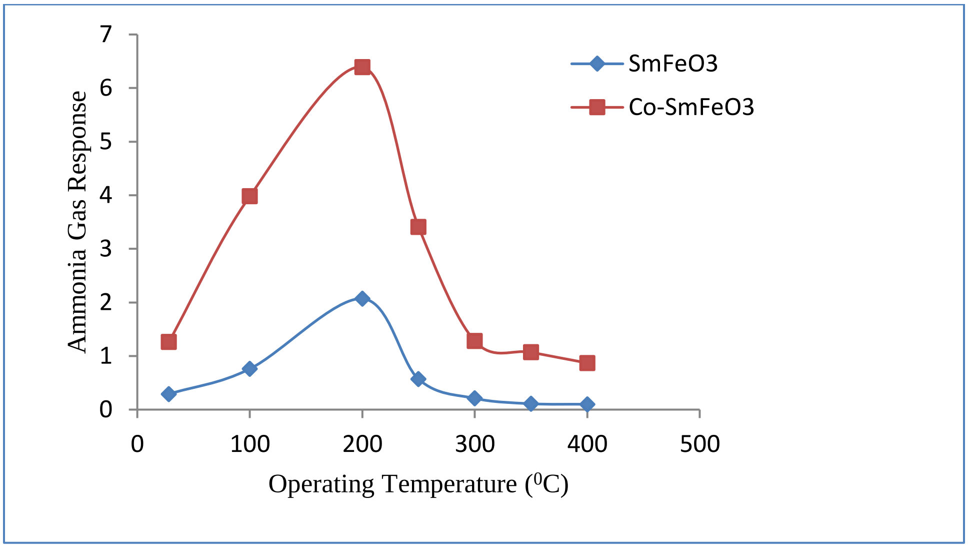

Fig. 3: Dependence of 50 ppm ammonia gas response on operating temperature for $SmFeO_3$ and Co-$SmFeO_3$ films.

Initial growth and then decay in gas response was observed with the increase in operating temperature. The maximum gas response 6.39 was obtained at optimal operating temperature of 200 ^{0}C. This variation in gas response with operating temperature is related to adsorption and desorption rates. Below optimal operating temperature, desorption rate is very small and above optimal operating temperature, desorption rate is high. Hence small change in resistance and thereby decrease in response at lower and higher temperatures was recorded.

The change in resistance of Co-$SmFeO_3$ film was monitored for 60 days and the results are graphically illustrated in Fig. 5. Negligible change in the resistance of sensor was observed indicating good stability and durability of Co-$SmFeO_3$ film.

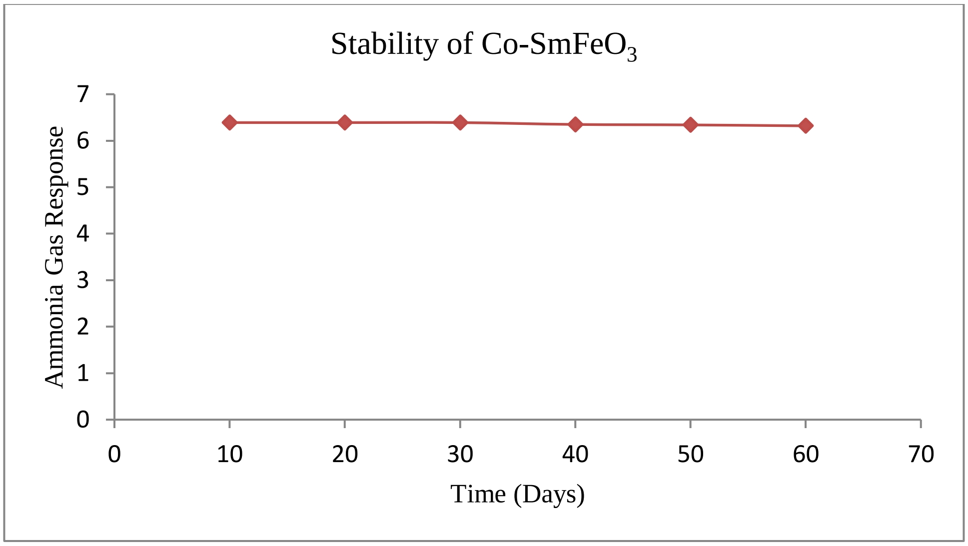

Fig. 4: Stability of Co-$SmFeO_3$ based sensor.

3.3. Ammonia gas sensing mechanism:

The most accepted gas sensing mechanism of p-type $SmFeO_3$ is described below. In presence of air, the adsorbed oxygen species extract the electrons from conduction band and get converted to O_2^-, $2O^-$ or O^{2-} depending on the temperature. Due to this, concentration of electron holes increases and the resistance of film decreases. When Co-$SmFeO_3$ film is exposed to ammonia gas, the extracted electrons returned back to the conduction band and the resistance of film increases. Eq. 1 depicts the chemical reaction of ammonia gas with chemisorbed oxygen [26].

$$2NH_3 + O^-{}_{(ads)} + O_2 \rightarrow 2NO_2 + 3H_2O + 5e^-. \quad (1)$$

3.4. Conclusion:

In this investigation, $SmFeO_3$ film was surface modified with Co by dipping it in cobalt chloride solution for 5 min. As prepared Co-$SmFeO_3$ film was selective to ammonia gas. To 50 ppm ammonia gas, response of Co-$SmFeO_3$ film was 6.39 at 200 ^{0}C which is three times more than that of $SmFeO_3$ film. The increased ammonia gas response is related to the additional oxygen vacancies induced by Co misfits.

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