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Impact of Palladium Decoration on the Performance of Co-$SmFeO_3$ Based Gas Sensor

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Abstract. The enhanced ammonia gas sensing properties of palladium decorated Co-modified $SmFeO_3$ (Co-SFO) are demonstrated here. Pristine $SmFeO_3$ thick films fabricated by screen printing technique were surface modified with Co by dipping method (dipping time 3 min) and identified as Co-SFO thick films. They showed maximum sensitivity to 50 ppm ammonia at 200 ^{0}C. In order to further increase its sensitivity, Co-SFO thick film was dipped into Palladium nitrate solution for 1 min, 2 min and 3 min. Surface morphology of as-prepared thick films was studied by FE-SEM. Formation of PdO phase and its uniform distribution over Co-SFO surface was confirmed from EDAX spectra. Gas sensing results revel that the sensitivity of Pd decorated Co-SFO thick films towards 50 ppm ammonia was increased. Moreover, decrease in operating temperature was also observed. Pd decorated Co-SFO thick film with dipping time 3 min has maximum sensitivity at lower operating temperature. The improved sensitivity at low temperature was attributed to the sensitization of palladium which was discussed in details.

Introduction

For the detection and monitoring of reducing gases like ammonia, semiconductor metal oxide based gas sensors are more effective as compared to conventional methods [1-3]. Till date, various semiconductor metal oxides like ZnO, TiO_2, SnO_2, $LaFeO_3$ and their composite systems have been continuously investigated as material for gas sensor [4-7]. Sensitivity, selectivity, optimal operating temperature and stability are the key parameters that determine the applicability of particular semiconductor metal oxide to a gas sensor. Surface morphology, surface to volume ratio, nature and amount of additives have strong impact on their gas sensing properties [8-10].

In the group of orthoferrites, $SmFeO_3$ is one of the potential rare earth orthoferrite that has been extensively reviewed for the detection of oxidizing gases [11-13]. Extremely low gas response due to small electrical conductivity and the chemical instability under reducing condition are the major issues associated with $SmFeO_3$ [14]. Adding the controlled amount of reducible dopants like cobalt to pristine $SmFeO_3$ is an effective approach adopted by many researchers in order to improve its gas response [15-16].

Noble metals like Palladium are well known effective oxidation catalyst [17]. Their special electronic structure, can introduce additional impurity levels into the band gap of semiconductor metal oxide. Doping of semiconductor metal oxide with noble metals can enhance the reactions occurring at the surface of gas sensor [18-20]. Therefore, noble metal decoration of nanocomposites could be an effective approach to further improve its gas sensing properties.

In previous works, the gas sensing properties Co surface modified $SmFeO_3$ thick films (dipping method) have been studied and reported that the film with dipping time 3 min exhibited the maximum response (21.07) to 50 ppm ammonia gas at 200^{0}C [21]. Moreover, good selectivity and response and recovery were also recorded. In continuation with this work, now Co-SFO thick films are decorated with palladium and investigated the effect of palladium noble metal on its ammonia gas sensing properties.

Experimental

Fabrication of Pd decorated Co-SFO thick films: Screen printing technique was adopted to fabricate Co-SFO thick films. Preparation of $SmFeO_3$ powder, fabrication of thick films and Co surface modification were described in our previous publications [21]. As-prepared thick films were dipped into palladium nitrate solution for 1 min, 2 min and 3 min. and identified as *Sample A, Sample B* and *Sample C*. The films were allowed to dry naturally for 24 hours and then fired at 550^0C for half an hour.

Characterization and Gas sensing tests of Pd decorated Co-SFO: X-ray diffraction pattern of $SmFeO_3$ powder was recorded by XPERT-PRO, PW-3071 X-ray diffractometer with Cu-Kα radiation of wavelength 1.54 Å and compared with standard powder diffraction file. The surface morphologies of Pd decorated Co-SFO thick films were investigated by field emission scanning electron microscope (JSM- 6380A, JEOL Japan) operated at 15 kV. To determine the elemental composition, energy-dispersive X-ray (EDAX) spectra of the samples were recorded.

Gas sensing performance of Pd decorated Co-SFO thick film was investigated using static gas-sensing setup. Thick film with electrical contacts is kept on heater in an enclosed chamber pre-filled with air. The desired temperature is maintained using temperature controller and sensor resistance in air is measured. Known volume of test gas is then injected into the gas chamber using syringe and sensor resistance in test gas is measured. Concentration of test gas was kept constant (50 ppm) and the operating temperature was varied from 27^0C to 400^0C.

Results and Discussion

X-Ray Diffraction study: Fig. 1 shows XRD pattern for the prepared $SmFeO_3$ powder and explained in earlier publications [21].

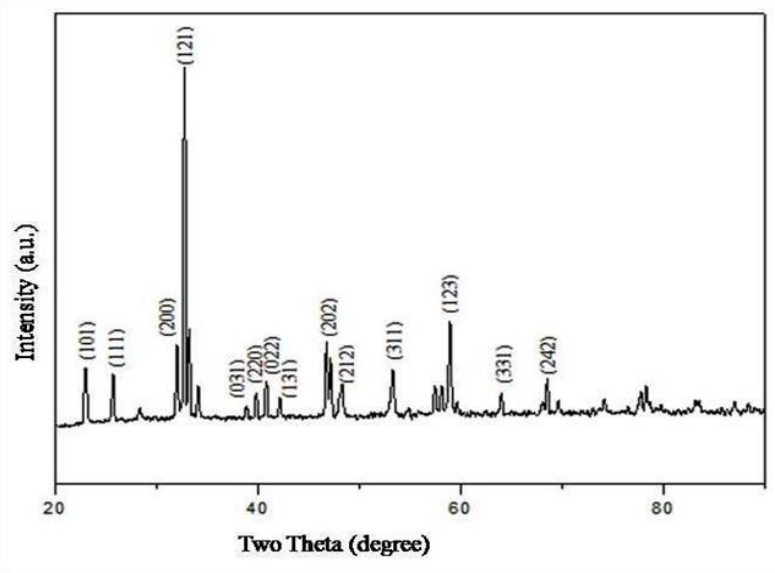

Fig. 1. XRD pattern of pure $SmFeO_3$ powder.

The narrow and sharp peaks in XRD pattern indicate crystalline nature of powder. The XRD pattern reveals that the diffraction peaks are well indexed to standard JCPDS card number 39-1490. The highest intensity peak corresponds to the lattice plane (121) and it was observed at 32.71^0. The presence of main peak at 32.71^0 confirms orthorhombic structure with Pnma space group for $SmFeO_3$ powder. Absence of any impurity peak confirms the purity of sample. The average crystallite size is calculated using Scherrer's formula

$$d = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

where, 'λ' is wavelength of X-ray, 'θ' is diffraction angle and 'β' is Full Width at Half Maximum (FWHM). The average crystallite size is estimated as d=50.08 nm.

Morphological analysis: Fig. 2(a-c) depicts the FE-SEM micrographs of Pd decorated Co-SFO thick films.

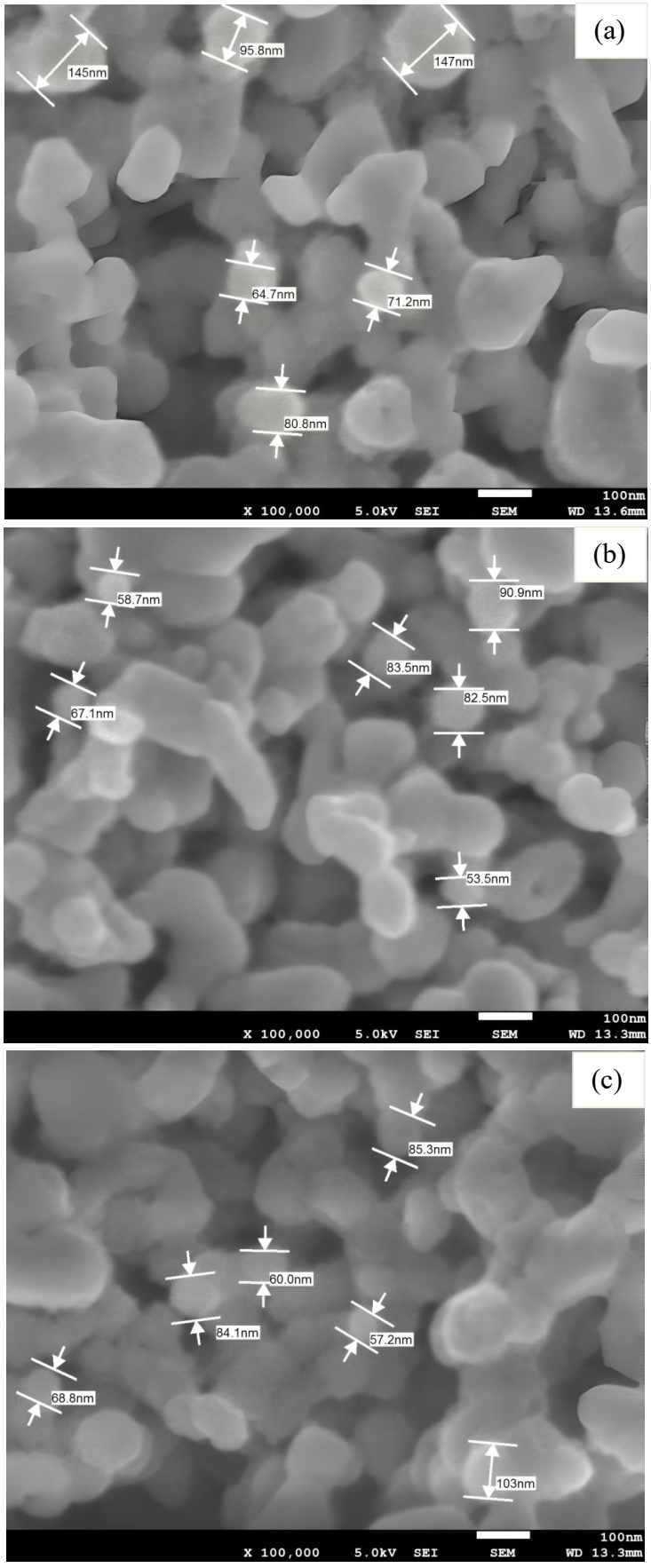

Fig. 2. FE-SEM images of (a) Pd decorated Co-SFO dipped for 1 min, (b) Pd decorated Co-SFO dipped for 2 min and (c) Pd decorated Co-SFO dipped for 3 min.

The films appear to be consists of wide range of particles which are distributed non-uniformly. Randomly oriented nanostructures with small spheres and interconnected particles were observed in all the films. In Fig. 2 (a), it is observed that the average grain size is about 100 nm. Fig. 2 (b) shows that the average grain size becomes 72 nm. Fig 2 (c) depicts that the average grain size is 74 nm. Thus FESEM results reveal that average grain size is around 72-100 nm. Due to the incorporation of Pd, grain size was observed to be decreased and results in large surface to volume ratio. Further such spherical nanostructured morphology with high porosity results in the increased in sensitivity.

Elemental Composition analysis: Fig. 3 (a–c) depicts the EDAX images of Pd decorated Co-SFO thick films. The presence of Pd element and its dispersion on the surface of film can be observed in EDAX mapping. Fig 4 shows EDAX mapping for Pd decorated Co-SFO thick film (dipping time 3 min). Pd is represented by a pink dot in the EDAX mapping. The EDAX analysis confirms the presence of only Sm, Fe, O, Co and Pd with no other impurities on Pd decorated Co-SFO thick films.

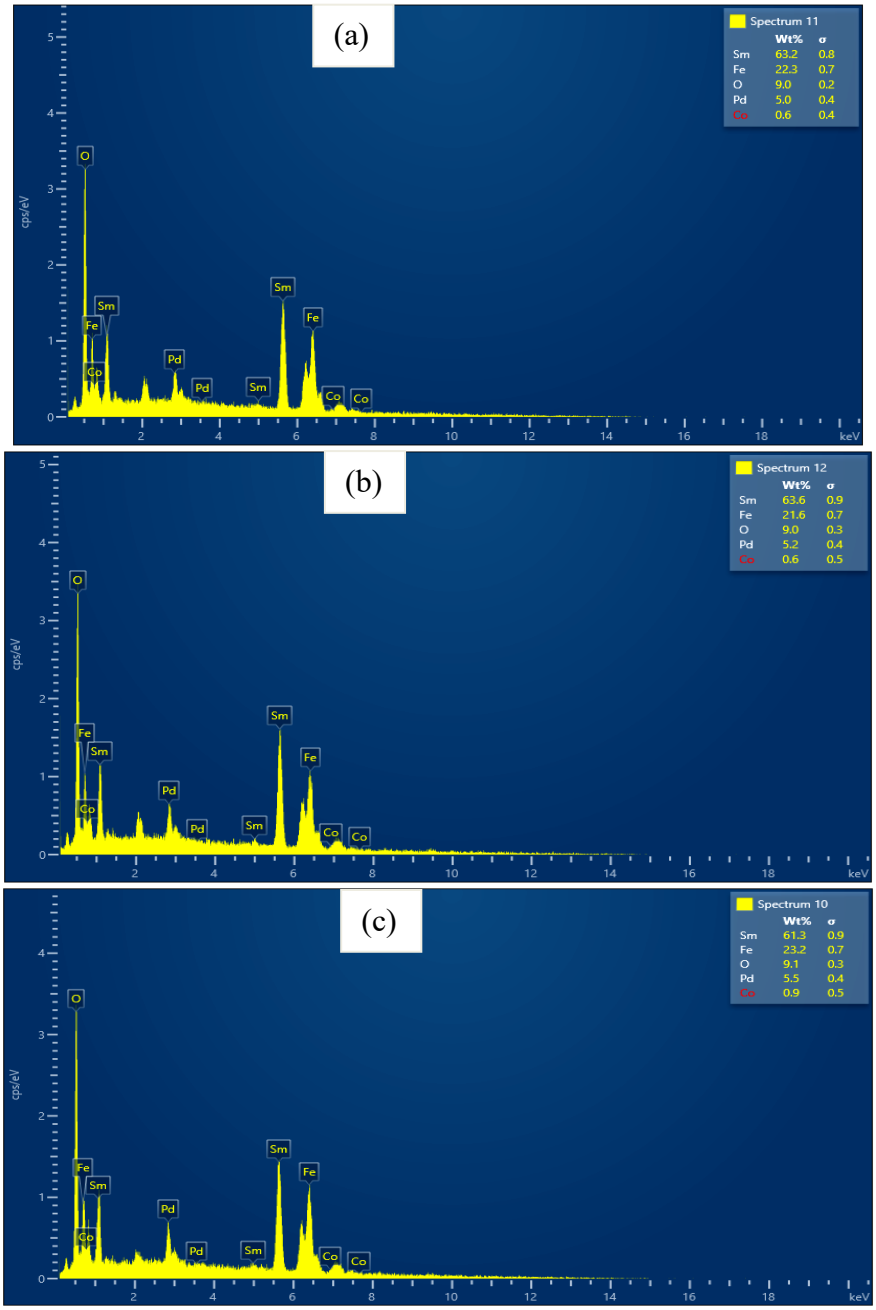

Fig. 3. EDAX images of (a) Pd decorated Co-SFO dipped for 1 min, (B) Pd decorated Co-SFO dipped for 2 min and (c) Pd decorated Co-SFO dipped for 3 min.

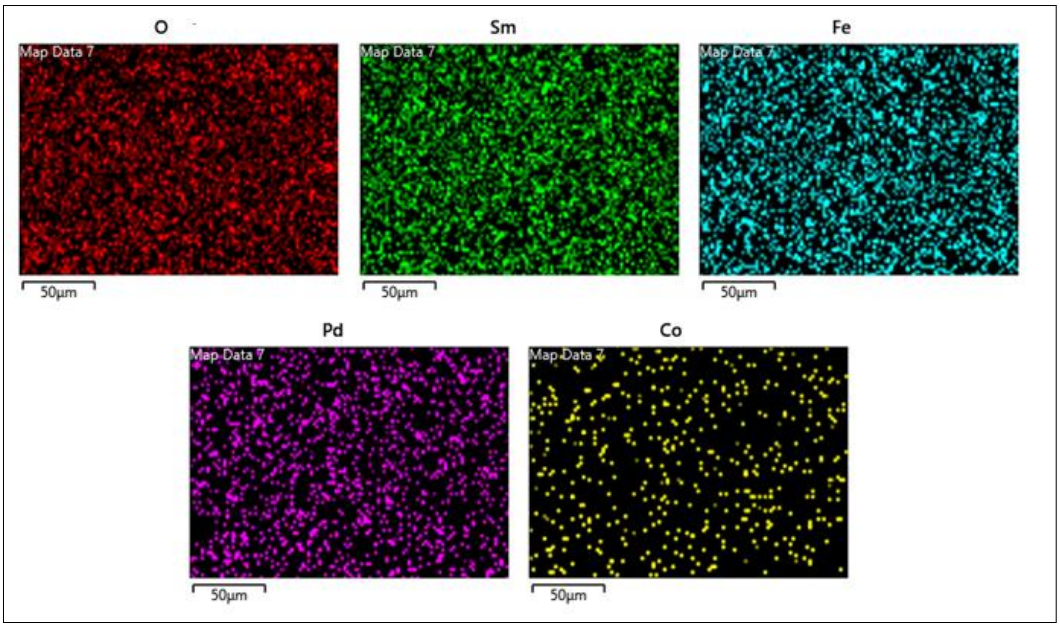

Fig. 4. EDAX mapping for Pd decorated Co-SFO (dipping time 3 min).

The wt % of Pd along with Sm, Fe, O and Ce are represented in Table 1. The result shows that maximum amount of Pd is incorporated on Co-SFO thick film for dipping time 3 min.

Table 1. wt % of elements present in Pd decorated Co-SFO thick films.

Material (wt %)	Dipping Time (min)		
	1 min	2 min	3 min
Sm	63.2	63.6	61.3
Fe	22.3	21.6	23.2
O	9.0	9.0	9.1
Pd	**5.0**	**5.2**	**5.5**
Co	0.6	0.6	0.9

Gas sensing performance: Generally gas response is determined to express the performance of gas sensor. For p-type semiconductor metal oxides, gas response is expressed as (R_g/R_a) where R_g and R_g represents resistance of semiconducting material in target gas and in air respectively [22]. In our earlier work, maximum gas response (21.07) towards 50 ppm ammonia gas at 200 ^{0}C was recorded for Co-SFO thick film [21]. In continuation to this work, the gas response of Pd decorated Co-SFO films (dipping times 1 min, 2 min & 3 min) to 50 ppm ammonia have been studied. After palladium decoration, response towards ammonia is increased. The maximum response values are 31.6, 32.02 and 38.65 for Pd decorated Co-SFO films with dipping times 1 min, 2 min & 3 min respectively. The corresponding optimal operating temperatures are 200 ^{0}C, 150 ^{0}C and 150 ^{0}C. This shows that the Pd decorated Co-SFO thick film (dipping time 3 min) has better ammonia gas response among all the investigated samples. This improved ammonia gas response is related to the catalytic property of palladium.

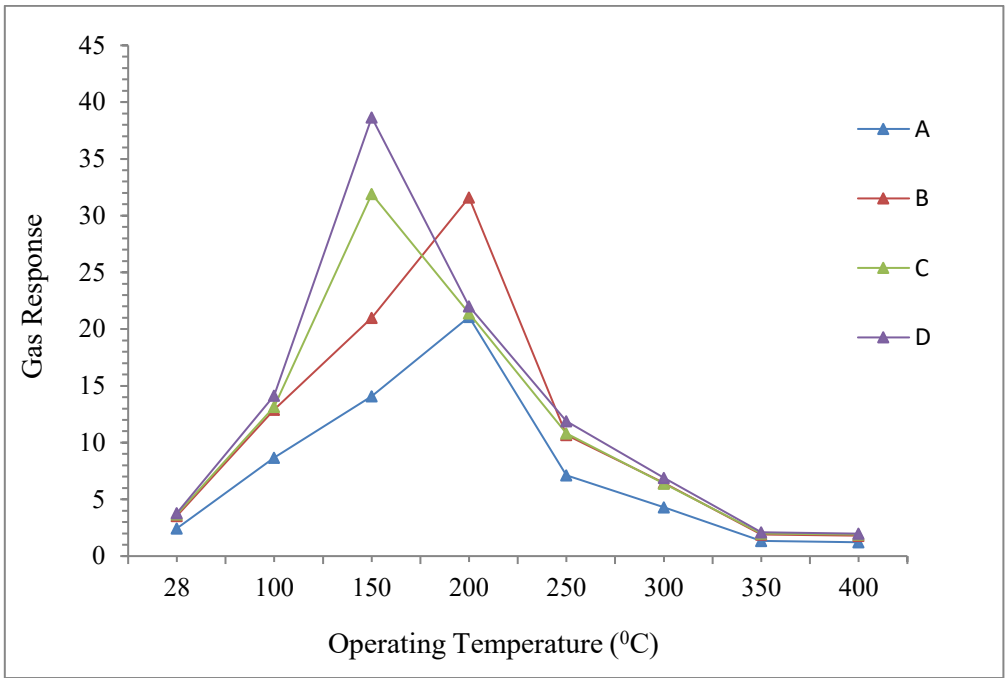

Fig. 5. Gas responses to 50 ppm ammonia as a function of operating temperature for (A) Co-SFO (B) Pd decorated Co-SFO dipped for 1 min, (C) Pd decorated Co-SFO dipped for 2 min and (D) Pd decorated Co-SFO dipped for 3 min.

Fig.5 represents the ammonia gas response of undecorated Co-SFO and Pd decorated Co-SFO (dipping times 1 min, 2 min & 3 min) samples as a function of operating temperature to 50 ppm ammonia gas. It is observed from Fig. 5 that, with the increase in operating temperature, the gas response initially increases and then decreases. Adsorption and desorption of gas molecules occurs simultaneously at sensor surface. At temperature lower than optimal temperature, desorption rate is very small whereas at temperature higher than optimal temperature, desorption rate is high. Hence small change in resistance and thereby decrease in response at lower and higher temperatures was recorded. For each sample, maximum response was obtained at temperature known as optimal operating temperature. In previous work, optimal operating temperature for Co-SFO was 200 ^{0}C which is now shifted to 150 ^{0}C for Sample B and Sample C. Moreover, same increase and then decrease pattern is also recorded for gas response when the operating temperature increases in the given range.

The amount of palladium loaded to Co-SFO surface strongly affects the gas response. Therefore, Co-SFO films dipped in palladium solution for different time intervals showed different responses towards 5o ppm ammonia gas. Fig. 6 depicts the ammonia gas responses as a function of dipping time. Palladium is an effective oxidation catalyst. Doping with palladium enhances the surface reactions occurring at sensor surface due to its sensitization effects. The sensitization effect of palladium is strongly affected by its concentration and dispersion on the surface of metal oxide [23]. As seen from Fig. 6, maximum gas response is obtained for dipping time 3 min indicating that concentration of Pd loaded on the surface of Co-SFO is optimum and well dispersed on the surface. Hence sensitization of Pd is pronounced for dipping time 3 min as compared to samples with dipping time 1 min and 2 min.

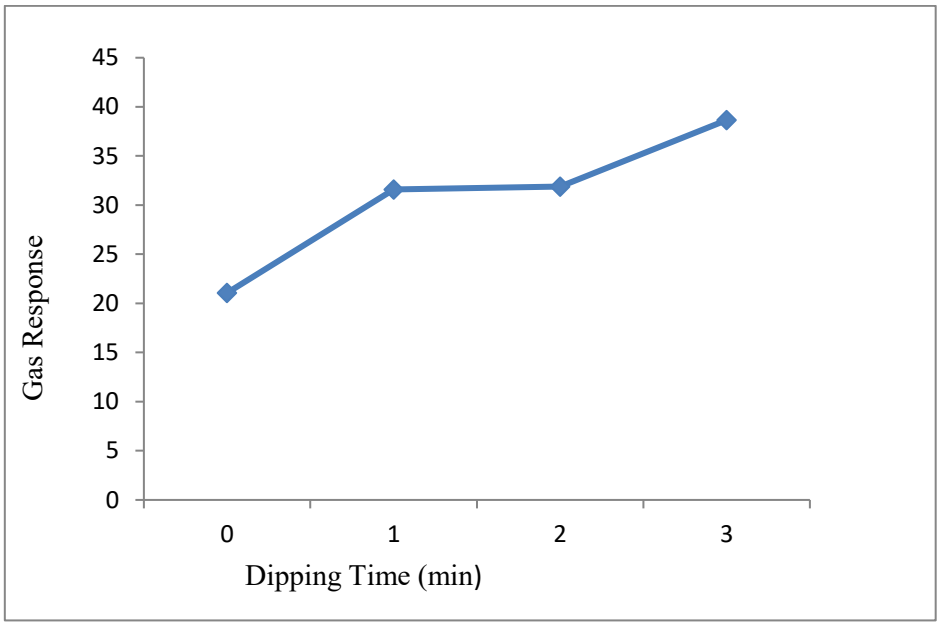

Fig. 6. Ammonia gas responses as a function of dipping time for Pd decorated Co-SFO dipped for 1 min, 2 min and 3 min

The selectivity nature of Pd decorated Co-SFO (dipping time 3 min) towards 50 ppm ammonia gas in the presence of other gases is also been investigated and the results are demonstrated in Table 2. Thus, the above results depict that the gas response of Pd decorated Co-SFO (dipping time 3 min) towards 50 ppm ammonia gas at 150 ^{0}C does not change in the presence of other investigated gases. Hence as-prepared Pd decorated Co-SFO (dipping time 3 min) has good selectivity. The enhanced selectivity towards ammonia may be related to the ionization energy of ammonia. Ammonia molecules have reduced ionization energy and therefore can quickly diffused into the sensing material surface.

Table 2. Response of Pd decorated Co-SFO (dipping time 3 min) towards 50 ppm ammonia gas in the presence of other gases

Material	Response towards 50 ppm ammonia gas in the presence of				
	50 ppm H_2	50 ppm LPG	50 ppm H_2S	50 ppm C_2H_5OH	50 ppm CO_2
Pd decorated Co-SFO (dipping time 3 min)	38.50	38	38.	37.50	38.65

The stability of Pd decorated Co-SFO (dipping time 3 min) is determined by measuring its change in resistance at 150 ^{0}C continuously for 90 days. The results are graphically illustrated in Fig. 7 and shows that negligible change in the resistance of sensor was observed. Hence sensor has good stability and durability.

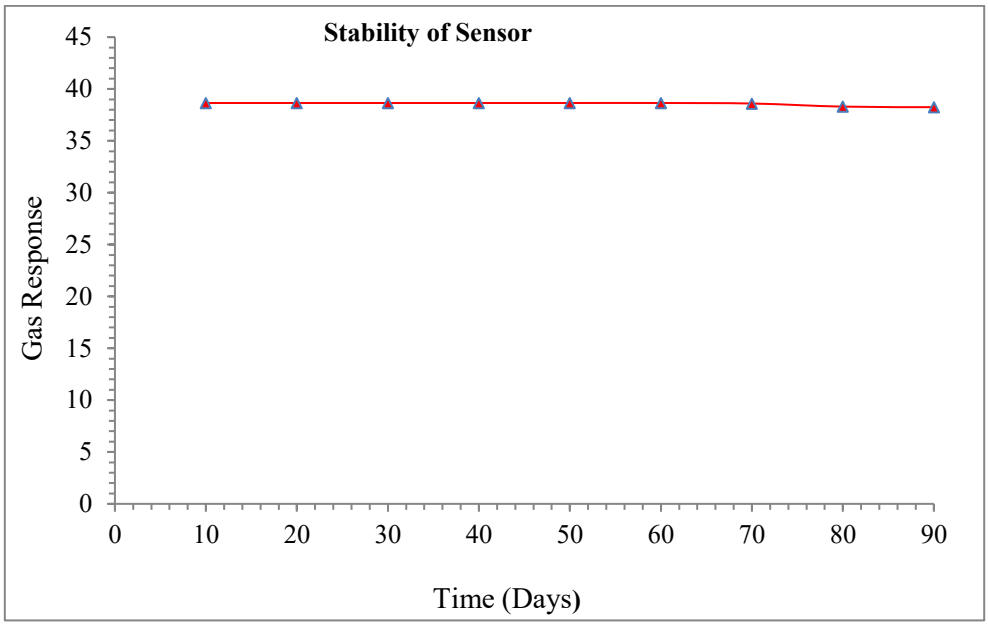

Fig. 7. Stability of Pd decorated Co-SFO thick film

The characteristics of recently reported various ammonia gas sensors are mentioned in table 3. Comparison with these ammonia sensor shows that the performance of as-prepared Pd decorated Co-SFO ammonia sensor is satisfactory. Therefore, Pd decorated Co-SFO can be a good material for detection of ammonia gas.

Table 3. Gas sensing performance of various ammonia sensors

Material	Gas concentration	Optimal operating temperature	Response	Ref.
Pd/WO_3 thin film	50 ppm	300^0C	43.6	[24]
ZrO_2 (0.125 M) thin film	500 ppm	100^0C	S= 60%	[25]
Ag-decorated TiO_2	20 ppm	25^0C	25.1	[26]
Graphene	1000 ppm	25^0C	S=18.5%	[27]
MoS_2/MWCNTs	150 ppm	Room Temperature	S=30%	[28]

Sensitization mechanism of Palladium: Ammonia sensing mechanism by semiconductor metal oxide is explained by many authors [24-28]. In air, electrons from Co-$SmFeO_3$ are captured by adsorbed oxygen species thereby forming the hole accumulation layer near the surface. During this process, oxygen species are converted to O_2^-, $2O^-$ and O^{2-} according to the temperature. When ammonia gas is inserted, ammonia reacts with oxygen species and ionizes into H_2O, N_2 and the captured electrons are released thereby decreasing the width of whole accumulation layer. The chemical reaction of ammonia gas with chemisorbed oxygen is depicted in Eq. 2 [25].

$$4NH_3 + 3{O_2}^-{}_{(ads)} \rightarrow 2N_2 + 6H_2O + 6e^-. \quad (2)$$

In Pd decorated Co-SFO thick film, the enhanced sensing performance towards ammonia gas may be the combined effect of chemical sensitization or electronic sensitization. Palladium ion (Pd^{2+}) has unoccupied d orbit and unpaired valence electron [30]. Palladium exists as PdO nanoparticles on the surface of Co-SFO in air and can rise the adsorption of oxygen in air. Since fermi level of PdO is larger than that of SFO, PdO becomes strong electron acceptor which traps more electrons thereby further decreasing the initial resistance of sensor. In chemical sensitization, also called spill-over effect, Pd nanoparticles also become active sites [27]. Palladium is an effective oxidation catalyst and can quickly oxidize ammonia molecules into corresponding atoms. Therefore, activation energy of surface reactions is reduced. The reduced activation energy also drops the working temperature of sensor. In presence of ammonia gas, Pd dissociates ammonia molecules into corresponding atoms. Then these dissociated atoms spill over from Pd to the surface of

semiconductor metal oxide. During subsequent spill over, dissociated atoms interact with chemisorbed oxygen species and released the trapped electrons to conduction band. By subsequent spill over, the number and the speed of electrons released to the host material increases.

Conclusion

All investigated Pd decorated Co-SFO thick films exhibited enhanced ammonia gas sensing properties as compared to Co-SFO thick films. Among them, Pd decorated Co-SFO (dipping time 3 min) produced highest gas response (38.65) to 50 ppm ammonia gas at 150 ^{0}C. Moreover this sensor has good stability. Thus addition of palladium not only increased sensitivity but also decreases the optimal temperature of the sensor. The observed decreased in optimal operating temperature of sensor is ascribed to the lower activation energy of surface reactions in presence of palladium. Palladium produces fast catalytic oxidation and additional reaction paths are available.

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