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Surface Modification of Cobalt doped Hydroxyapatite Thick Films via Swift Heavy Ion Irradiations for CO and CO_2 Gas Sensing Application

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Abstract:
In the present investigation, Swift Heavy Ion irradiation (SHI) has been successfully utilized to modify the structure and surface morphology of cobalt doped Hydroxyapatite (HAp) thick films for CO and CO_2 gas sensing application. Nano-crystalline Co-HAp powder is used to prepare sensor matrix in the form of thick films by means of screen printing technique. Furthermore, Co-HAp thick films are irradiated using Ag^{7+} ions (100 MeV) with ion fluence of $3x10^{11}$ and $3x10^{13}$ ions/cm^2. Structural evolutions are investigated by means of X-ray analysis and surface morphology is visualized by means of SEM analysis. A detail gas sensing study is carried out to determine operating temperature, response recovery time and gas uptake capacity to assess the stable performance of sensor. This investigation reveals that the SHI irradiated Co-HAp ($3x10^{11}$ ions/cm^2) film showed enhancement in gas sensing characteristics in comparison to pristine film. The study is remarkable to note that Co-HAp ($3x10^{11}$ ions/cm^2) film shows enhancement in CO & CO_2 gas sensing behavior at lower operating temperature 150^{o}C and 135^{o}C respectively.

Key words: Keywords: Hydroxyapatite, Swift Heavy ions (SHI) irradiation, Thick films, Gas Sensor, XRD and SEM.

1. Introduction

Environmental protection policy for most of the countries in worldwide is oriented towards the regulation, precise measurement and control of the hazardous and toxic gases. The gas sensor devices have acquired importance in monitoring the level of toxic gases. The detection of these gases in domestic application is a requirement as far as safety is concerned This has stimulated considerable interest to develop simple and cost-effective chemical sensors for the detection of these gases. Up till now, the metal oxide semiconductors such as SnO_2, TiO_2, ZnO, have been widely investigated as a gas sensing materials [1]. However, the combination of organic and inorganic nano-bio-ceramic Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp], materials has been proposed as an effective approach to achieve complementary properties and dynamic effects for hazardous gas sensing application.

Recently, our group has been reported the enhancement in CO and CO_2 gas sensing properties of pure hydroxyapatite thick films, irradiated by Ag^{7+} ions with energy 100 MeV [2-3]. In this work, the operating temperatures for CO & CO_2 gases are observed to be 195°C and 165°C respectively. Generally, the gas sensor with maximum gas response at lower operating temperature is being preferred in various applications. In this regards, number of attempts have been carried out by doping the metallic species, such as Pt, Pd, Au, Ag, Fe, Co, etc., with base semiconductor and metal oxide systems in order to improve better sensor characteristics [4]. Hence, for continuation of this work, an attempt has been carried out to study the dual effect by adding Co metal ion in HAp sensor matrix as well as surface modification by Swift Heavy Ion irradiation.

In the present investigation, we report the effect of swift heavy ion irradiation, on the structural, morphological and gas sensing properties of screen printed Co-HAp thick films at variable ion fluences. Pre & post irradiation characterization have been carried out using XRD and SEM analysis. The systematic study of CO and CO_2 gas sensing properties of the sensor is investigated from the aspects of gas response, response/recovery time & gas uptake capacity.

2. Experimental

2.1 Material Synthesis

Nano-ceramic HAp used in the present study is synthesized by wet chemical precipitation route. The detail synthesis process of HAp is reported in our earlier work [2]. Ion exchange process is carried out using synthesized nano ceramic HAp powder (1 gm) are dispersed in 100 cm^3 of 25 mmol dm^{-3}

$Co(NO_3).6H_2O$ solution with different molar concentration (0.008, 0.01, 0.05M) of batch solution. All the batches are thoroughly shaken for 5 hours and settled for overnight and washed with double distilled water and finally dried in air oven at 100°C for 10 hours. Ion exchanged nanoceramic Co-HAp powders are used for film preparation by using screen printing technique [3]. The ion irradiation is carried out using Ag^{7+} ions with energy 100 MeV from Pelletron accelerator at IUAC, New Delhi. The samples are irradiated with the ion fluence of $3x\ 10^{11}$ to $3\ x\ 10^{13}$ ions/cm^2.

The gas sensing characterization is carried out on pristine and irradiated Co-HAp thick films using homebuilt gas characterization unit reported in our earlier work [3]. The ratio of change in resistance of the sensor in presence of air and test gas, are noted followed by Gas response (%) calculation using the following formula;

Gas response S (%) = [Rg – Ra] / Ra * 100 (1)

The structural and surface characterization of pristine and ion irradiated Co-HAp film are carried out using XRD, and SEM. Wherein, X-ray diffraction pattern was recorded with a Bruker AXS Germany (Model D8 Advanced) having CuKα (λ= 1.5405 Å) incident radiation. The XRD peaks are recorded in the 2θ range of 20°–60°. Surface morphology of the pristine & irradiated thick film samples is visualized by means of Scanning Electron Microscope (Vega TESCAN).

3. Results and Discussion

3.1. X-ray Analysis

Fig. 1 (A-C) shows the XRD profiles of pristine and ion irradiated Co-HAp thick films with various ion fluences. The XRD phase identification is performed by using JCPDS standard XRD card (09-432), (01-1278) for HAp and cobalt respectively. All the peaks, corresponding to the 2θ values reveal the formation of hexagonal phase of the HAp film with crystalline nature. The peaks present at 2θ value of 38.68° and 41.09° are due to Co ions which are indicated by (*). It is observed that the intensities of all characteristics peaks are goes on decreasing with increase in ion fluence. This decrease in peak intensity may be due to structural damage produced at higher fluence. The crystallite size for pristine samples is found to be 30 nm and that for irradiated Co-HAp films with a fluence of $3x10^{11}$ ions/cm^2, and $3x10^{13}$ ions/cm^2 are found to be 35 nm, and 49 nm respectively.

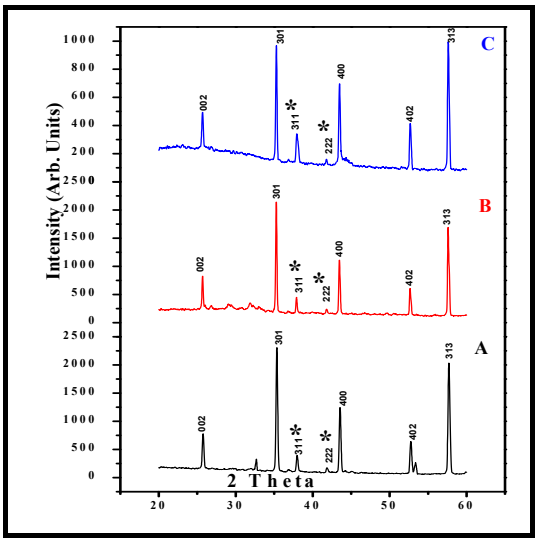

Fig.1 (A-E). XRD patterns of (A) Pristine Co-HAp and with ion fluence (B) $3x10^{11}$ ions/cm^2 (C) $3x10^{13}$ ions/cm^2.

3.2. SEM Analysis

Fig. 2(A-C) shows the surface morphology of pristine and ion irradiated films as a function of ion fluence. Fig. 2(A) shows the pristine film in which the small grains of variable size are seen. When the sample is irradiated with ion fluence $3x10^{11}$ ions/cm^2, the surface is split and collate with each other and more microporosity is shown in film surface as presented in fig. 2(B). Since, these micropores located on the Co-HAp ($3x10^{11}$ ions/cm^2) surface, should increase the active surface area as well as the presence of loose and porous structure can also assist for faster gas diffusion and removal process thus possibly enhancing the gas sensing performance [5]. Furthermore, increase in ion fluence ($3\ x\ 10^{13}$ ions/cm^2) at an excessive level the particles shows large cluster type structure as observed in fig. 2(C).

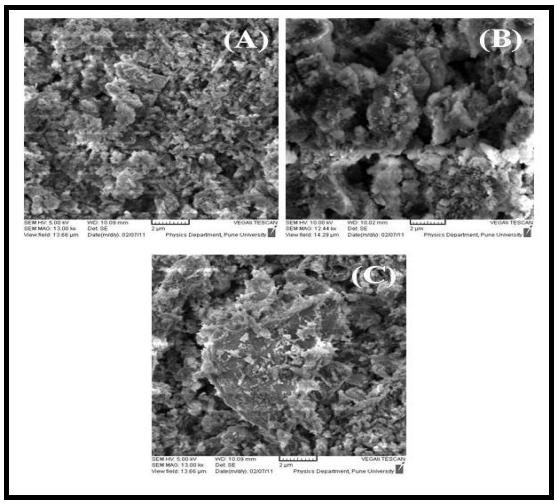

Fig.2 (A-C). SEM Images of (A) Pristine Co-HAp and with ion fluence (B) $3x10^{11}$ ions/cm^2 (C) $3x10^{13}$ ions/cm^2.

3.4. Sensing performance of HAp Thick Film Sensor

Fig. 3(A-B) shows the gas response of pristine and ion irradiated Co-HAp thick film as a function of operating temperature upon exposure to CO and CO_2 gas concentration of 1000 ppm.

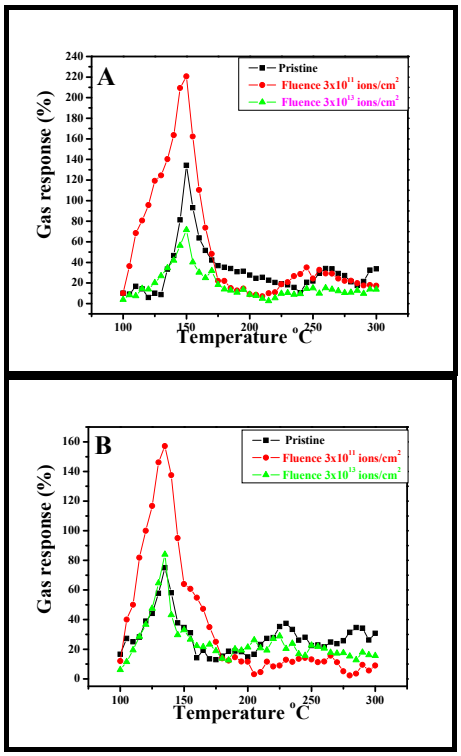

Fig 3 (A-B) Variation in Gas response as a function of temperature for Pristine and ion irradiated films with ion fluence 3x10^{11} ions/cm^2 and 3x10^{13} ions/cm^2 of (A) CO gas (B) CO_2 gas.

Fig. 3(A) shows the behavior of CO gas response as a function of temperature for pristine and ion irradiated Co-HAp thick films. The virgin as well as modified films show similar behavior with a maximum change in resistance occurring at 150°C. This ensures the lower operating temperature for pristine and modified sensors which is found to be unaffected by ion irradiation process. The pristine Co-HAp film shows the CO gas response of 135 at an operating temperature 150°C. However, in case of modified films gas response is found to be the highest 220 for the Co-HAp film irradiated with 3x10^{11} ions/cm^2. The observed higher response in the present study is attributed to the formation of microporous structure of Co-HAp (3x10^{11} ions/cm^2) film as shown in Fig. 2 (B). However, the films irradiated with higher fluence 3x10^{13} ions/cm^2 show decrease in gas response of the order of 72. In case of CO_2 gas sensing, for pristine and ion irradiated Co-HAp thick film we found similar observations. The Co-HAp thick film with ion fluence 3x10^{11} ions/cm^2 shows the maximum gas response 156 at a relatively lower operating temperature 135 °C.

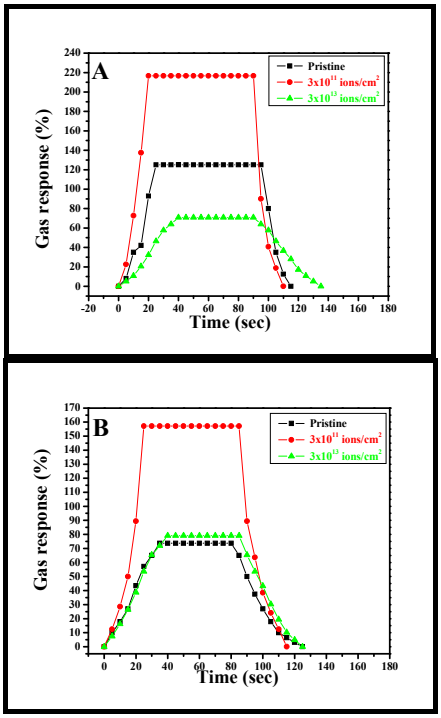

Fig 4 (A-B) Response and Recovery time of pristine and ion irradiated Co-HAp thick films for 1000 ppm of (A) CO gas (B) CO_2 gas.

Fig. 4(A-B) shows the response and recovery characteristics of the pristine and ion irradiated Co-HAp films to 1000 ppm of CO and CO_2 gases at the operating temperature 150°C and 135°C. As can be seen from Fig. 4(A-B), the sensor responds very rapidly after introduction of CO and CO_2 gas and get recovers when it is exposed to air. The Co-HAp film (3x10^{11} ions/cm^2) shows the response time of the order of ~20 and 25 s and the recovery time of ~20 and 30 s for CO and CO_2 gases respectively. Fig. 5 (A-B) shows the linear variation in gas response with variable CO and CO_2 gas concentration in the range of 500 ppm to 25,000 ppm. It is observed that as the concentration of CO and CO_2 gases increases, the gas response increases linearly in the beginning and later it becomes saturated. For pristine samples the gas uptake capacity is found to be 19000 and 13000 ppm for CO and CO_2 gases respectively. The gas uptake capacity is found to be maximum for samples irradiated with 3x10^{11} ions/cm^2 fluence up to 24000 and 21000 ppm for CO and CO_2 gases. This indicates that Ag^{7+} ion irradiated with 3x10^{11} ions/cm^2 fluence creates more sites available for gas adsorption by the way of increasing the porosity, whereas, higher ion fluence damages the HAp structure leading to lower porosity and ultimately converting the matrix from crystalline to amorphous nature on the surface.

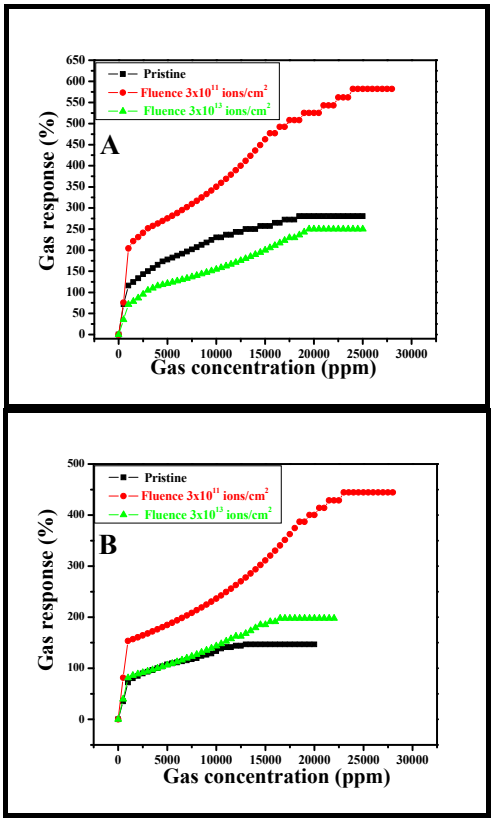

Fig 5 (A-B) Gas uptake capacity pristine and ion irradiated Co-HAp thick films for (A) CO gas (B) CO_2 gas.

Moreover, the possible mechanism for adsorption of CO and CO_2 gas on HAp surface is understood as follows: The hydroxyapatite surface can be characterized by unique properties like several P-OH groups &/or several ionic species like Ca^{2+}, PO_4^{3-} & OH^- along with porosity. Wherein the ions, namely protons (H^+), oxide ions (O^{2-}) or the lattice hydroxyl ions (OH^-) being played an important role to determine the reactivity with gas molecules and contribute to conductivity at elevated temperature [3]. The OH^- ions play a vital role for gas adsorption process. Laghizizil et al reported the following reaction between neighboring two OH- ions [6].

We assumed that, formation of oxygen (O^{2-}) molecules on HAp surface interact with CO gas molecules producing CO_2 and releasing electrons. Furthermore, a CO_2 molecule again reacts with oxygen molecules according to the following reaction;

$$OH^- + OH^- \longrightarrow O^{2-} + HOH \quad (2)$$

CO_2 disintegrates in CO and O at elevated surface temperatures, thereby

$$CO + O^{2-} \longrightarrow CO_2 + 2e^- \quad (3)$$

$$CO_2 + O^{2-} \longrightarrow CO_3^{2-} \quad (4)$$

Thus, the formation of CO_3^{2-} molecules is found to be responsible for sensor application of HAp [2-3].

4. Conclusion

Swift heavy ion irradiation has been effectively employed to improve the structural, morphological and gas sensing properties of cobalt doped HAp thick films. The structural and morphological investigations are carried out by means of XRD and SEM. Repeatability test confirm the relatively lower operating temperature (150°C and 135°C) for CO and CO_2 gases. The response recovery time is observed to be minimum for fluence $3x10^{11}$ ions/cm^2 compared to pristine and other fluence. Moreover, the gas uptake capacity of Co-HAp ($3x10^{11}$ ions/cm^2) film is enhanced up to 24,000 and 21,000 ppm for CO and CO_2 gases respectively. The study concludes that swift heavy ion irradiations plays vital role in modification of surfaces which alters the gas sensing behaviour of sensor matrix.

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