

# Effect of substrate temperatures on CO<sub>2</sub> gas sensing properties of spray deposited La<sub>2</sub>O<sub>3</sub> thin films

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## Abstract

Carbon dioxide gas (CO<sub>2</sub>) sensing properties of La<sub>2</sub>O<sub>3</sub> thin films synthesized by spray pyrolysis deposition method are studied. La<sub>2</sub>O<sub>3</sub> thin films are characterized for their structural, surface morphological, optical and electrical properties and used for CO<sub>2</sub> gas response measurements. SEM analyses indicates porous surface morphology, to which CO<sub>2</sub> gas is found to be sensitive. The deposited La<sub>2</sub>O<sub>3</sub> films are crystalline with pronounced orientation along (110) plane, uniform and adherent to glass substrate. From optical absorbance studies, the optical band gap is obtained as 4.2 eV. With this morphology, the maximum response of 15 % at 623 K is recorded on exposure to 400 ppm of CO<sub>2</sub> gas.

**Keywords:** CO<sub>2</sub> gas sensor, La<sub>2</sub>O<sub>3</sub>, Spray pyrolysis method, Thin film.

## Introduction

In the field of chemical sensor, for more than five decades it has been known that the electrical conductivity of semiconductors varies with the composition of the gas atmosphere surrounding them. This mechanism of the detection will help to monitor hazardous gases and to detect the threshold level of gases present in the atmosphere. However, these sensors showed poor performance with respect to the sensitivity at low concentrations of gases, selectivity and long-term stability [1,2]. The gas sensing devices based on organic materials, such as polypyrrole, polyaniline, and metaphthalocyanine, have gas sensitivity at room temperature, but their long response time due to the orderly structure limits their usage [2,3]. Many metal oxides show good sensitivities towards various gases like CO, NH<sub>3</sub>, NO<sub>x</sub>, SO<sub>x</sub>, alcohol vapor and liquefied petroleum gas (LPG) [3-5]. Gas sensors have a great influence in many areas such as environmental monitoring, domestic safety, public security, automotive applications, air conditioning in airplanes, space crafts, houses, and in sensors networks [2, 3]. Due to this huge application range there is need of cheap, small, low power consuming and reliable solid state gas sensors, which is overcome the metal oxide sensors drawbacks, and improve the sensitivity, selectivity and stability.

The main application of gas sensor is to detect hazardous gases that can harm people when it is spread to atmosphere. So gas sensor are used to detect a leaking of hazardous gas to the atmosphere [6, 7]. The sensing properties of various semiconductor metal oxide like CuO, SnO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, and In<sub>2</sub>O<sub>3</sub> in the form of thin or thick films have been studied [4-8]. The n- type metal oxides such as SnO<sub>2</sub>, ZnO, and WO<sub>3</sub> show high and quick response to number of hazardous and toxic gases like CO<sub>x</sub>, NO<sub>x</sub>, NH<sub>3</sub> and LPG [5-7]. Amongst these, it has been seen that the global warming and climate change are mainly due to the increase of carbon dioxide (CO<sub>2</sub>) in air atmosphere. Thus, the detection and control of CO<sub>2</sub> concentration in environment is necessary. Besides, CO<sub>2</sub> sensors can be used in fields of air-quality monitoring, agricultural production, clean energy technologies, engine exhausts and chemical industry[9]. Consequently, there is a need for development of cost effective sensors to monitor CO<sub>2</sub> gas. Most of the p-type oxides like NiO, Cr<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> are good catalysts and exhibit selective oxidation of particular gases and hence show essential characteristic of selectivity towards certain gases, compared to other gases [10-13]. In that, La<sub>2</sub>O<sub>3</sub> is an environment friendly and highly stable p-type semiconductor metal oxide has been used in various applications such as gas sensors, catalysts, supercapacitors, batteries, electromagnetic, luminescence devices and biomedicine [14-21]. Jinesh et al [22] reported use of nanostructured La<sub>2</sub>O<sub>3</sub>/Si layers for CO<sub>2</sub> gas sensing.

In this paper, the structural and morphological characteristics of spray deposited La<sub>2</sub>O<sub>3</sub> thin films are studied. The gas sensing properties of La<sub>2</sub>O<sub>3</sub> thin films are studied using various parameters such as selectivity, sensitivity and stability.

## Methods

La<sub>2</sub>O<sub>3</sub> films were deposited on glass substrates by chemical spray pyrolysis technique. The substrates were cleaned, before deposition with freshly prepared chromic acid, followed by detergent solution and distilled water. The precursor solution was prepared using 0.1 M concentration of lanthanum nitrate and urea (AR grade) in double distilled water. The atomization of the solution into a spray of fine droplets was

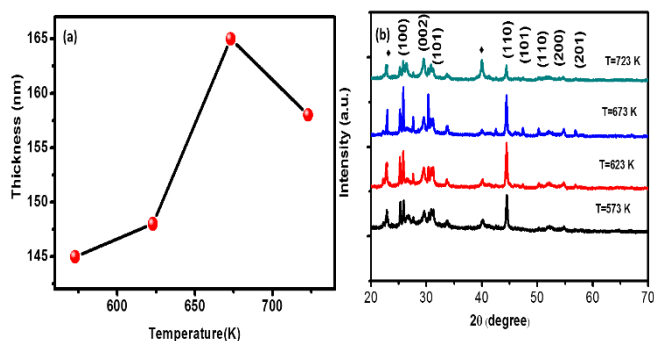
carried out by a spray nozzle, with the help of compressed air as a carrier gas [23]. During optimization of the process parameters, the substrate temperature was found to be the most important parameter in film preparation for gas sensor applications. The substrate was kept at various temperatures ranging from 573 to 723 K. Thickness of deposited thin film measured by gravimetric weight difference method. The structural properties were studied by using Philips X-ray diffraction (XRD) equipment with monochromatic high intensity CuK  $\alpha$ - radiation. The microstructural study was accomplished using a scanning electron microscope (SEM) JEOL JSM-6360. Optical absorption study was carried out using Shimadzu UV- 1800 spectrometer with glass substrate as a reference. In the present study, the sensor response of the films was determined using Eq. (1) as CO<sub>2</sub> gas possesses the properties of reducing gas. The electrical resistance of La<sub>2</sub>O<sub>3</sub> thin films in air and in the presence of CO<sub>2</sub> gas was measured to evaluate the gas response, defined as follows:

$$S \% = \frac{R_g}{R_a} \times 100 \quad (1)$$

where, R<sub>a</sub> is the resistance of the film in air and R<sub>g</sub> is that upon exposure to CO<sub>2</sub> gas.

### Result and discussion

La<sub>2</sub>O<sub>3</sub> films were deposited at four different substrate temperatures viz. 573, 623, 673 and 723 K. **Fig. 1 (a)** shows the thickness variation of La<sub>2</sub>O<sub>3</sub> thin films with respect to substrate temperature. From fig. 3.2, it is seen that initially thickness increases with increase in substrate temperature, attains a maximum thickness (195 nm) at 673 K and then decreases for the higher substrate temperatures. This can be explained as initially, lower substrate temperature (573 K) may not be sufficient to decompose the sprayed droplets from the solution and this results into a low thickness. At a substrate temperature 673 K, the decomposition occurs at the optimum rate resulting in the terminal thickness of 195nm. The decrease in La<sub>2</sub>O<sub>3</sub> film thickness at higher substrate temperatures may be due to a higher evaporation rate of the initial ingredients of the solution [24].

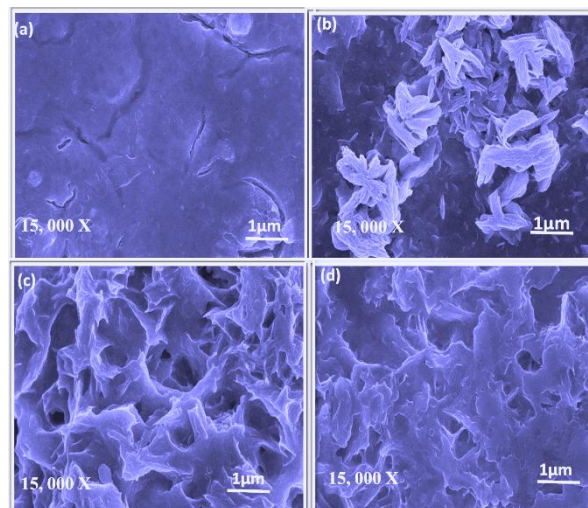


**Fig. 1(a and b)** Variation in film thickness, and XRD patterns of La<sub>2</sub>O<sub>3</sub> thin films with substrate temperatures.

**Fig. 1 (b)** shows X-ray diffraction patterns of La<sub>2</sub>O<sub>3</sub> thin films deposited on glass substrate for different substrate temperatures from 573 to 723 K. It is seen that films are polycrystalline with the sharp and strong diffraction peaks which are well indexed to La<sub>2</sub>O<sub>3</sub> crystalline phase (space group: p-3m1 (164), a = 4.0570 Å, b = 4.0570 Å, c = 6.3749 Å) in agreement with hexagonal crystal structure (JCPDS No.:00-040-1281). The peaks indexed using the symbol

“ ♦ ” are impurity peaks of lanthanum carbonate. It is seen that as the substrate temperature increases, the peak intensity increases and (110) peak shows relatively higher peak intensity for the films deposited at 673 K. The increase in peak intensity may be due to the sufficient increase in supply of thermal energy for recrystallization and the grain growth with temperature [21,25]. La<sub>2</sub>O<sub>3</sub> is crystallized in two phases as cubic-La<sub>2</sub>O<sub>3</sub> (c-La<sub>2</sub>O<sub>3</sub>) and hexagonal-La<sub>2</sub>O<sub>3</sub> (h-La<sub>2</sub>O<sub>3</sub>). The c-La<sub>2</sub>O<sub>3</sub> is stable at low temperature and h-La<sub>2</sub>O<sub>3</sub> is stable at high temperature. The h-La<sub>2</sub>O<sub>3</sub> phase has higher dielectric constant, low leakage current and more crystalline than c-La<sub>2</sub>O<sub>3</sub> phase [26]. The h-La<sub>2</sub>O<sub>3</sub> phase is more useful than c-La<sub>2</sub>O<sub>3</sub> in applications such as gas sensor [23],supercapacitor [24] and catalysis [22]. Therefore, deposition temperature 623 K was optimized to obtain the crystalline and uniform h-La<sub>2</sub>O<sub>3</sub> thin film.

**Fig. 2** shows the scanning electron micrograph (SEM) images of La<sub>2</sub>O<sub>3</sub> thin films deposited at different substrate temperatures and magnification of X 50,000. It is seen that **(Fig. 2 (a))** the surface of La<sub>2</sub>O<sub>3</sub> film contains cracks spread over entire surface. Such cracks are due to low deposition temperatures (<523 K) where solid films are formed from droplets at hot substrate surface. **Fig. 2 (b)** shows the cracks-like morphology is converted in to the uniform sheet-like morphology. Film growth mechanism leads to the byproduct gases to be captured within the grown film forming voids. For higher deposition temperature (623 K) surface becomes rough, which changes from sheet-like to porous morphology as shown in **Fig. 2 (c)**. Above 673 K, the grains start to agglomerate at 723 K **(Fig. 2 (d))**[27].



**Fig. 2** Scanning electron micrographs of La<sub>2</sub>O<sub>3</sub> thin films deposited by spray pyrolysis method at (a) 573, (b) 623, (c) 673, and (d) 723 K substrate temperatures and magnification of 50,000 X.

**Fig. 3 (a)** shows the UV–Visible optical absorption spectra of the sprayed La<sub>2</sub>O<sub>3</sub> thin films obtained by varying the substrate temperature. The light absorption of La<sub>2</sub>O<sub>3</sub> thin films in the wavelength ranging from 290 to 850 nm was evidently high. As the substrate temperature increases, thickness of the deposited film also increases, due to which the absorption also changes. All films show a wide absorption band edge up to

300 nm, which is in agreement with the results obtained by Yadav et al [27]. The required parameters for semiconductor solid-state gas sensors are small activation energy and a large band gap. For solid-state gas sensor at operating temperature ( $T > 573$  K), the optimized band gap must be higher than 2.5 eV. The optical absorption data are analyzed using the following classical relation [24].

$$\alpha = \frac{A(E_g - hv)^n}{hv} \quad [2]$$

where,  $A$  is a constant,  $E_g$  is the separation between bottom of the conduction band and top of the valence band,  $h\nu$  is the photon energy and  $n$  is an order. The value of  $n$  depends on the probability of the transition; it takes values as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. Fig. 3 (b) shows that variation of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) for  $\text{La}_2\text{O}_3$  thin films. The direct band gap energy is determined by extrapolating the linear part of the plot to zero energy (Absorption coefficient  $\alpha = 0$ ) and is varied between 3.7 to 4.2 eV, which is agreement with previously reported literature data [25]. The difference in the observed optical properties of  $\text{La}_2\text{O}_3$  thin films may result from some stoichiometric variation of  $\text{La}_2\text{O}_3$  films deposited at different temperatures

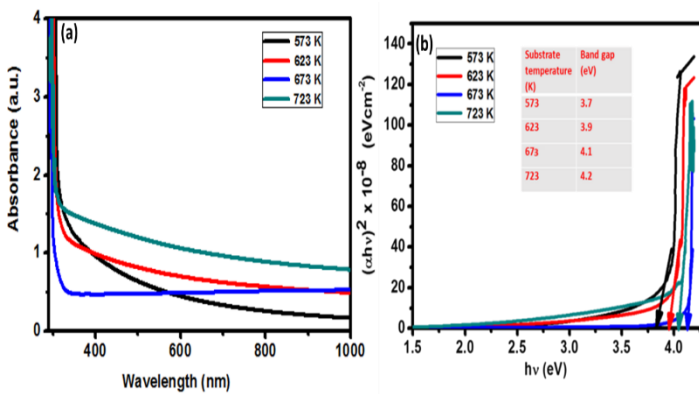


Fig. 3 (a) Absorbance spectra, and (b) plot of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) for  $\text{La}_2\text{O}_3$  thin films deposited at different substrate temperatures.

### CO<sub>2</sub> gas sensing study

$\text{La}_2\text{O}_3$  sensor is exposed to  $\text{CO}_2$  gas at various temperatures from 523 to 673 K. The optimum operating temperature of  $\text{CO}_2$  sensor is 623 K as shown in Fig. 4 (a). In a p-type semiconductor metal oxide, like  $\text{La}_2\text{O}_3$  [23] and  $\text{Cr}_2\text{O}_3$  [5], holes are majority charge carriers. As the temperature increases the resistance of  $\text{La}_2\text{O}_3$  surface decreases. The thermally excited electron comes from the valence band. When this surface is exposed to air, the oxygen from the air is adsorbed on  $\text{La}_2\text{O}_3$  surface by trapping electrons from surface. This process increases the charge carriers due to which resistance of the sensor decreases. When  $\text{CO}_2$  reducing gas molecule is introduced it further reacts with adsorbed oxygen and gets chemisorbed by giving electrons to the oxygen and thereby  $\text{La}_2\text{O}_3$  lattice. This increase in electrons causes the recombination of electrons-holes and results in increase of sensor resistance. On desorption of this  $\text{CO}_2$  molecule from  $\text{La}_2\text{O}_3$  surface, the charge carriers (holes) in the accumulation layer are restored and cause decrease in the sensor resistance [5]. The sensitivity of these sensor increases with increasing

operating temperature obtaining maximum value and then decreases with further increasing in operating temperature. These behavior based on the adsorption and desorption kinetics on the surface of  $\text{La}_2\text{O}_3$ . If the operating temperature is relatively low, the chemical activity of  $\text{La}_2\text{O}_3$  is low which leads the low response and due to high temperature the some of the gas molecule escape from the surface before reaction because of strong thermal motion due to high temperature, thus responses decrease. Therefore the optimum temperature is required for good the response [5].

The dynamic gas response characteristics of the sensor at gas concentration of 400 ppm for different temperatures is shown in Fig. 4 (b). The maximum response of 15 % is observed at 400 ppm gas concentration. The important parameter is response and recovery time, which is calculated under 400 ppm concentration of  $\text{CO}_2$  gas. Fig. 4 (c) shows the response time of  $\text{CO}_2$  sensor, decreasing from 168 to 58 s and the recovery time of  $\text{CO}_2$  sensor increases from 287 to 78 s. The ability of a sensor to respond to a certain gas in the presence of other gases is known as selectivity.

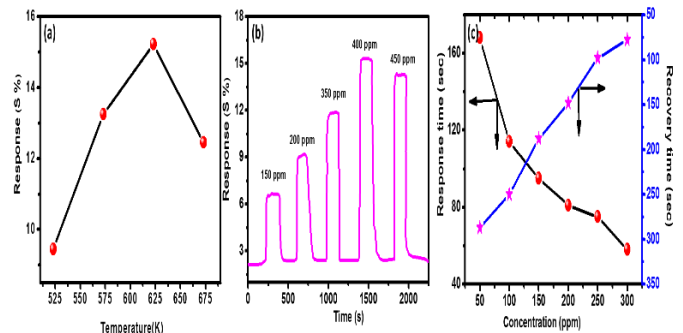


Fig. 4 (a) Variation of gas response of  $\text{La}_2\text{O}_3$  thin film for 400 ppm of  $\text{CO}_2$  gas at different operating temperatures, (b) dynamic response of  $\text{La}_2\text{O}_3$  thin film under various concentrations of  $\text{CO}_2$  gas, and (c) response and recovery time periods for  $\text{La}_2\text{O}_3$  thin film at different  $\text{CO}_2$  gas concentrations.

The selectivity study of  $\text{CO}_2$  gas sensor with respect to other gasses such as  $\text{N}_2$ , LPG at 623 K are shown in Fig. 5 (a). The gas response for  $\text{CO}_2$  is greater than that of the other gasses at the same concentration of 300 ppm.

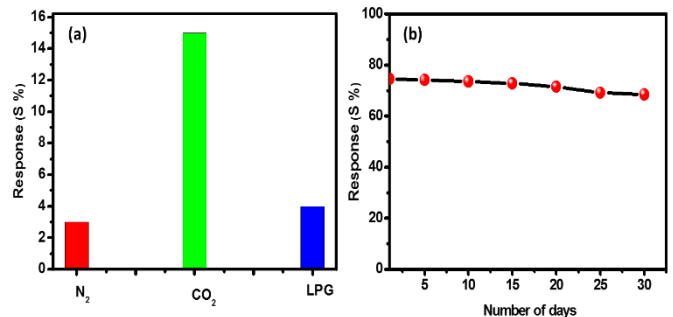


Fig. 5 (a) Comparative gas response of  $\text{La}_2\text{O}_3$  towards  $\text{CO}_2$ , LPG and  $\text{N}_2$  gas and (b) stability study of  $\text{La}_2\text{O}_3$  thin film at operating temperature of 623 K for 30 days.

To confirm the stability of  $\text{La}_2\text{O}_3$  sensor the responses at 300 ppm over months (Fig. 5 (b)). Therefore, stability of this material is good enough to detect  $\text{CO}_2$  over a long time.

## Conclusions

The spray deposited  $\text{La}_2\text{O}_3$  thin films are used to analyze the structural, morphological and optical properties.  $\text{La}_2\text{O}_3$  thin films shows hexagonal, crystalline nature with porous morphology. The optical study shows band gap various from 3.7 to 4.1 eV.  $\text{CO}_2$  gas sensing studies reveal that the films show p-type conductivity and exhibit a fairly good sensor response 15 % observed, when exposed to reducing  $\text{CO}_2$  gas at 623 K and 400 ppm concentration.

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