ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Structural, Morphological And Vapour Sensing Properties Of Spray Deposited CeO_2 Thin Film.

S Hemalatha[1,2]*, and G Priyamvada[1,2].

[1]Centre for Nanotechnology and Advanced Biomaterial (CeNTAB), SASTRA University, Thanjavur – 613 401, Tamilnadu, India.
[2]School of Electrical & Electronics Engineering, SASTRA University, Thanjavur – 613 401, Tamilnadu, India.

Abstract

Cerium oxide (CeO_2) thin films were deposited on glass substrate using home built spray pyrolysis technique under optimized spray deposition conditions. The structural, optical, morphological and vapour sensing properties were investigated. XRD pattern reveals the CeO_2 thin film was in polycrystalline with fluorite face centered structure. The formation of thin film with closely packed spherical nanoparticles was observed from SEM images and the particle size ranges from 20 to 30 nm. The film shows good optical transparency in visible region. The formaldehyde vapour sensing property of CeO_2 film was carried out using glass test chamber which was maintained at ambient temperature by chemiresistive method with a fast response and recovery time of 22 and 60 s respectively.

Keywords: Spray pyrolysis, Cerium oxide, Thin film, Formaldehyde, Chemiresistive.

Corresponding author

INTRODUCTION

Formaldehyde (HCHO), an organic compound that is volatile in nature is enormously utilized in manufacturing the household's products like paints and detergents. It is also associated with numerous health risk factors and further it has been found as the major carcinogenic agent causing cancer to human [1,2]. The Occupational Safety and Health Standards (OSHA) Board have some Permissible Exposure Limits (PELs) for various chemicals to which the workers are exposed in their workplace, considering their health. As per OSHA, for an 8h time weighted average (TWA), the PEL for HCHO is 0.75 ppm and considering the case of short-term exposure limit (STEL) for a duration of 15 mins TWA, the standard second PEL has been set as 2 ppm [3]. When exposed beyond the PEL, it causes respiratory diseases, immune disorders, central nervous system damage and blindness [4]. Therefore, there is a need for cost effective detection of formaldehyde vapour.

On searching for a simple, highly sensitive, attractive and cost effective way of detecting formaldehyde, one can make use of various metal oxide such as ZnO [5], SnO_2 [6], NiO [7], and TiO_2 [8]. Moreover, they have higher potential to be employed in real situations and their sensitivity to ppm and sub-ppm levels of HCHO are really appreciable. But these sensors operate well at higher temperature which can be a drawback as it needs a heater to be integrated with it making things complex design and high cost. Hence ambient temperature operated chemiresistor type is required.

As one of the most attractive rare earth material, Cerium oxide (CeO_2) has become a great interest due to its unique properties which is suitable for wide range of applications such as in solid oxide fuel cells, catalysts, and oxygen sensor as well as corrosion protection [9]. CeO_2 is a wide band gap material with a band gap value of 3.2 to 3.6 eV and has higher dielectric constant, chemical stability, high refractive index, high ionic and electronic conductivity [10]. CeO_2 is one of the most important material which exhibits better oxygen affinity when it is in fluorite cubic structure [11]. A number of different techniques were available to obtain CeO_2 thin films such as chemical vapor deposition [12], magnetron sputtering [13], flame spray pyrolysis [14], sol-gel [15] and e-beam evaporation [16]. Among these techniques spray pyrolysis technique is cost effective, simple, does not require high quality substrate materials and vacuum. In the present work, CeO_2 thin films were deposited by spray pyrolysis technique and it's morphological, optical, structural and vapour sensing characteristics were analysed and investigated.

MATERIALS AND METHODS

Preparation of sensing elements

The CeO_2 thin films have been deposited on glass substrate by using spray pyrolysis system (HOLMARC, HO-SPLF-01C) consisting of syringe pump. Initially 0.02 M of Cerium nitrate (III) hexahydrate ($CeN_3O_9.6H_2O$, 99.99% purity, Sigma-Aldrich) salt was taken and dissolved in deionized water was used as precursor solution. The glass substrates were cleaned with deionized water and placed onto the heater which was maintained at 250 ^oC. Then the prepared precursor solution was loaded into the glass syringe pump and the deposition parameters were optimized as given in Table 1. For each cycle of deposition, 5 s of spray time and 10 s of break time were maintained. When the compressed air flow reaches the nozzle of syringe pump, the solution was sprayed on the preheated substrates as a fine mist which undergoes thermal decomposition to form CeO_2 thin films. The pyrolytic reaction of CeO_2 thin film formation is given in Eq. (1),

$$Ce(NO_3)_3.6H_2O \rightarrow CeO_2 + 3NO_2 \uparrow + 6H_2O \uparrow + \frac{1}{2}O_2 \uparrow ---------(1)$$

Characterization

The structural properties of CeO_2 thin film were investigated using X' Pert Diffraction system (XRD) with CuKα radiation. The morphology of the film surface was carried out through field emission scanning electron microscopy (FE-SEM, JEOL-6701F, Japan). The optical properties of CeO_2 thin film were investigated using UV-Vis spectrophotometer in the wavelength ranges from 300 to 800 nm.

ISSN: 0975-8585

Table 1: Optimized spray deposition parameters.

Parameters	Values
Precursor	Cerium nitrate (III) hexahydrate (0.02 M)
Syringe pump nozzle diameter	0.3 mm
Solution flow rate	1 mL min^{-1}
Compressed air pressure	2 bar
Substrate to spray nozzle distance	23 cm
Spray angle	90^o
Substrate temperature	250 ^oC

Vapour sensing studies

The formaldehyde (HCHO) vapour sensing characteristics of CeO_2 thin film was examined using 1.5 L capacity of home build glass test chamber at the ambient temperature. It is supported by a septum provision, outlet port, film resistance measurement and vacuum pump. The calibrated concentration of liquid formaldehyde was injected through the septum provision in the glass test chamber by using a chromatographic syringe. Then the created HCHO vapour was removed with the help of vacuum pump which is connected to the test chamber and the changes in electrical resistance of CeO_2 thin film was noted.

RESULTS AND DISCUSSION

Structural studies

The X-ray diffraction (XRD) spectra of CeO_2 thin films were shown in figure 1. The diffractogram of CeO_2 thin film reveals polycrystalline in nature with fluorite face centered cubic structure which was compared with the standard JCPDS card [34-0394]. The formation of (1 1 1) plane orientation was observed from the obtained peak. The average crystallite size of CeO_2 thin film was calculated from the preferential plane using the Debye-Scherrer formula [17]. It was found to be 9 nm for CeO_2 thin films.

$$D = \frac{k\lambda}{\beta.\cos\theta} ---------- (2)$$

Where k is the shape factor (0.94), λ is the wavelength of X-ray (1.5406 Å), β is the full width at half maxima (FWHM) and θ is the angle of diffraction.

Morphological analysis

The scanning electron micrograph of as deposited CeO_2 thin films was shown in figure 2. It indicates that the thin film is of closely packed with spherical in shape. Also few agglomerated particles were observed and may be due to temperature effect. The corresponding crystallite size distribution is in the range of 20 to 30 nm.

Optical studies

The optical absorbance and transmittance spectrum of CeO_2 thin films were shown in figure 3. The peak absorption wavelength was obtained at 320 nm and became almost constant towards the visible region whereas the corresponding intensity of absorption peak was obtained at 0.9. Here, the deposited CeO_2 thin film shows good optical transparency (~38%) in the wavelength region of 320 to 800 nm.

Formaldehyde sensing studies

At ambient temperature, vapour sensing studies were carried out by home built glass test chamber. When the film was exposed to dry air atmosphere at ambient temperature, the oxygen molecules were adsorbed on the surface of the film by trapping electron and from the conduction band. This chemisorbed oxygen ions will increase the surface electrical resistance of CeO_2 film and is taken as base line resistance. As such, while exposing the CeO_2 film to formaldehyde vapour, the adsorbed oxygen species will be removed from the surface of the film by reduction reaction. This in turn decreases the surface resistance of CeO_2 thin film which leads to formaldehyde vapour detection. The response of the film towards HCHO vapour was calculated from the following relation

$$S = \frac{(R_a - R_g)}{R_g} \times 100 ---------- (3)$$

Where R_a is the resistance of thin film before the injection of targeted vapour, R_g is the resistance of thin film after the injection of targeted vapour and S is the response of the film.
The sensing scheme is given in equations 4 & 5.

$$O_2 + e^- \xrightarrow[CeO_2 surface]{} O_{2(ads)} ---------- (4)$$

$$HCHO + O^-_{2(ads)} \xrightarrow[CeO_2 surface]{} CO_2 \uparrow + H_2O \uparrow + e^- ---------- (5)$$

The change in resistance and response of CeO_2 thin film for different concentration of HCHO vapour was shown in figure 4 (a). As a result, the concentration of formaldehyde vapour increases there is a drastic decrease in resistance of CeO_2 thin film from 27 GΩ to 10 GΩ. Similarly the response increases from 43% to 310% which was maintained at room temperature.

For CeO_2 thin film, the transient resistance response for different concentration of formaldehyde vapour was plotted and shown in figure 4 (b). The curve indicates that there was a change in resistance when the film was exposed to formaldehyde vapour resulting in rapid response of the film. It might be due to the nanocrystallite present on the film surface which would enhance the rate of the reaction.

The response time and recovery time for HCHO vapour with various concentrations were plotted and shown in figure 5 which are defined as the time required to reach 90% and 10% of change in the film resistance from its base line resistance. The response time and recovery time for CeO_2 film were found to be 22 and 60 s respectively towards 100 ppm concentration of HCHO vapour.

The sensing response of CeO_2 thin film towards various reducing vapours like Diethanolamine, acetone, xylene, ethanol and formaldehyde were carried out at ambient temperature. Among those reducing vapour, film shows good sensing response to formaldehyde vapour.

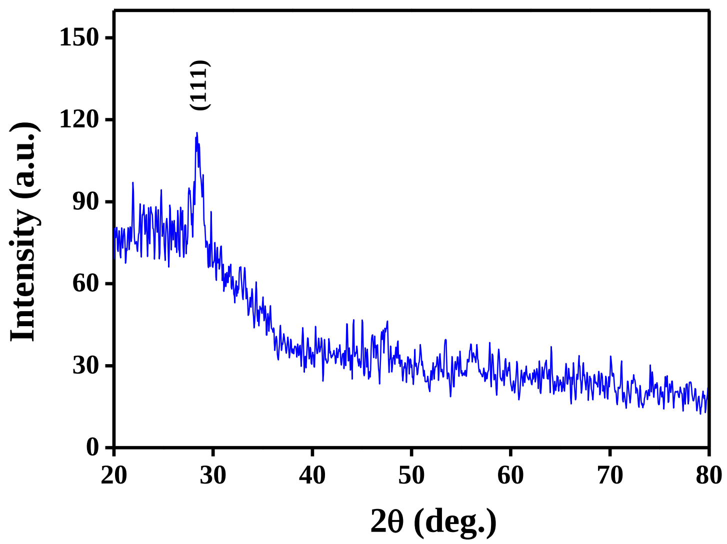

Figure 1: XRD pattern of pure CeO_2 thin film.

ISSN: 0975-8585

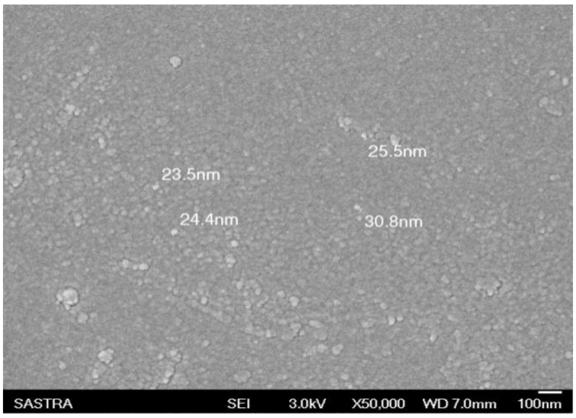

Figure 2: Scanning electron micrograph of CeO_2 thin film.

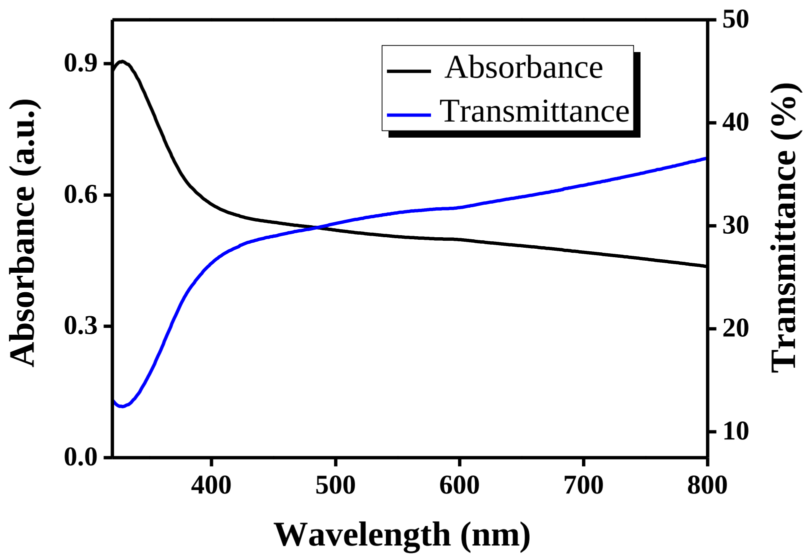

Figure 3: Optical absorbance and transmittance spectrum of spray deposited CeO_2 thin film.

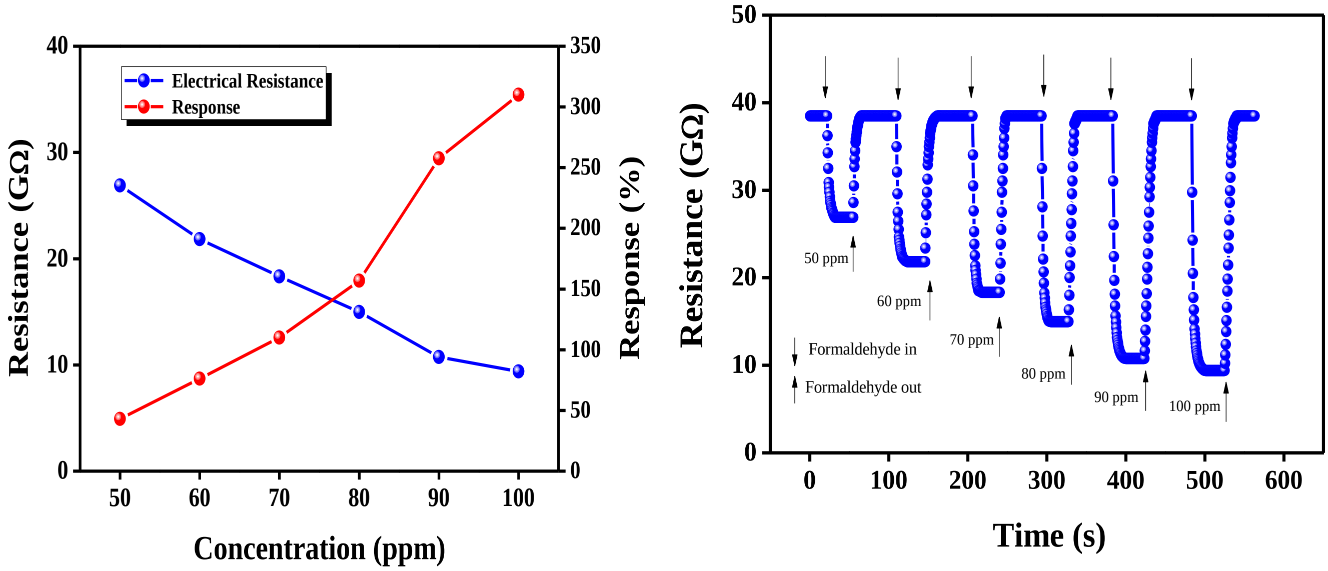

Figure 4 (a) Response and resistance characteristics as a function of concentration, (b) Transient response of different concentration for formaldehyde vapour.

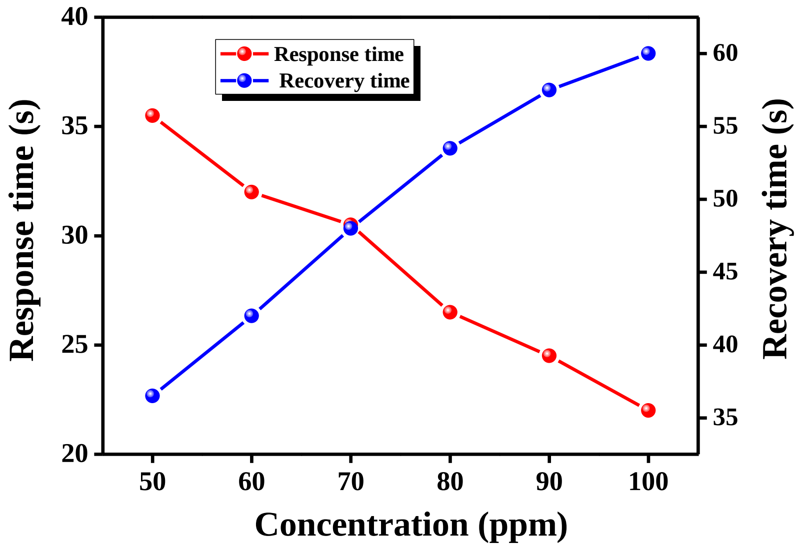

Figure 5: Response time and recovery time for different concentration of formaldehyde vapour.

CONCLUSION

The CeO_2 thin films were deposited on glass substrate using spray pyrolysis technique which exhibits polycrystalline in nature with fluorite cubic face centered structure. The average crystallite size was found to be 9 nm and from the SEM micrographs, it was observed that the crystallite size distribution ranges from 20 to 30 nm whereas the CeO_2 thin film has spherical nanoparticles. The film shows good transient response to formaldehyde vapour when compared with other vapour.

ACKNOWLEDGEMENT

Authors thanks the SASTRA University for providing all facilities and to Dr. B. G. Jeyaprakash, Research supervisor for his valuable suggestions and support towards the completion of work.

REFERENCES

[1] Po- Ren Ch, Chun- Ta T, Ming- Tsun K, Chia- Yen L. Sensors 2013;13:4468- 4484.
[2] Asif Ali K, Rifaqat Ali KR, Alam N, Shakeeba S. Sens Actuators B 2015;211:419-427.
[3] Vaishnav VS, Patel SG, Panchal JN. Sens Actuators B 2014;202:1002-1009.
[4] Shiwei L. Sens Actuators B 2011;156:505-509.
[5] Prajapati CS, Sahay PP. Sens Actuators B 2011;160:1043–1049s.
[6] Zhou X, Fu W, Yang H, Mu Y, Ma J, Tian L, Zhao B, Li M. Mater Lett 2013;93:95-98.
[7] Dirksen JA, Duval K, Ring T. Sens Actuators B 2001;80:106.
[8] Gu L, Zheng K, Zhou Y, Li J, Mo X, Patzke GR, Chen G. Sens Actuators B 2011;159:1-7.
[9] Bhosale AK, Tarwal NL, Shinde PS, Kadam PM. Solid State Ionics 2009;180:23-25.
[10] Suresh R, Ponnuswamy V, Mariappan R. Ceram Int 2014;40:13515-13527.
[11] Suresh R, Ponnuswamy V, Mariappan R. Mat Sci Semicon Proc 2014;21:45-51.
[12] Vargas-Garcia JR, Beltran-Romero L, Tu R, Goto T. Thin Solid Films 2010;519:1-4.
[13] Guhel Y, Bernard J, Boudart BS. Microelectron Eng 2014;118:29-34.
[14] Choowong Ch, Anusara W, Sirichai P. Ceram Int 2011;37:1459-1463.
[15] Xiaofei Qu, Dandan Xie, Lei Gao. Mat Sci Semicon Proc 2014;26:657-662.
[16] Porqueras I, Person C, Corbella C. Solid State Ionics 2003;165:131.
[17] Samue MS, Lekshmi B, George KC. SB Academic Review 2009;16:57-65.