Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 12 (16): 1738-1741, 2012
ISSN 1812-5654 / DOI: 10.3923/jas.2012.1738.1741

Influence of Mn Doping on Physical Properties of Nanostructured CeO_2 Thin Films

C.H.S.S. Pavan Kumar, R. John Bosco Balaguru and B.G. Jeyaprakash
School of Electrical and Electronics Engineering, Centre for Nanotechnology and Advanced Biomaterials, SASTRA University, Thanjavur-613 041, Tamil Nadu, India

Abstract: Cerium oxide is a multi-application material due to its wide band gap (3.6 eV) and lattice parameter matching similar to silicon. Its high dielectric constant, ionic conductivity and ferromagnetic nature makes to utilize as insulating layer in transistors, solid oxide fuel cells and spintronic application, respectively. In the present study, thin films of cerium oxide and Mn doped cerium oxide films have been prepared on glass substrates by homemade spray pyrolysis unit. X-ray diffraction pattern analysis shows peak broadening upon doping and indicates a decrease in grain size. The influence of Mn doping on electrical properties was also analyzed and reported.

Key words: Cerium oxide, manganese, electrical properties

INTRODUCTION

Ever, since its discovery in 1803 by Berzelius, Cerium Oxide (CeO_2) has been utilized in numerous applications. In power electronics sector, one of the important requirements for the power devices includes higher blocking voltages. Wide band-gap semiconductors like CeO_2 can be a potential replacement of silicon for achieving this requirement (Shenai *et al*., 1989). Thin films of cerium oxide can also be used as intermediate buffer and protective layers in high temperature superconductors and superconductor thin films, respectively (Konstantinov *et al*., 2000). The resistance of metals and alloys can also be improved to high temperature oxidation by employing ceria thin films (Wang *et al*., 2000). CeO_2 films being highly transparent also finds application in smart window devices (Elidrissi *et al*., 2000). When doped with glass, CeO_2 has the capability of absorbing UV and can be used for protecting light- sensitive materials (Debnath *et al*., 2007). Due to its unique ability to gain/lose oxygen, CeO_2 can also be employed as oxygen sensors (Gupta *et al*., 2009). CeO_2 thin films as humidity sensors have also been reported (De Souza *et al*., 2007). The effect of doping ceria also alters its physical properties which can be put to use in several applications. These properties apart from many other factors also depend on type of dopant. Reports have established that electrodes in solid oxide fuel cells incorporate Sm doped ceria while Pr and Mn doped are used in applications such as oxygen permeable ceramics (Takamura *et al*., 2009). The sintering temperature can also be reduced by doping ceria with Mn (Pereira *et al*., 2005). In this study, the variation of structural and electrical properties on CeO_2 thin films has been studied. Many methods to deposit thin films have been established each having its own merits and de-merits. The choice of choosing a particular technique mainly determines the quality of the film deposited. The thickness of the films also varies with the type of deposition. Literature survey shows that various deposition techniques such as sol-gel (Wu *et al*., 2006), magnetron sputtering (Tang *et al*., 2007), electron beam evaporation (Debnath *et al*., 2007) and spray-pyrolysis (Wang *et al*., 2000) have been reported to deposit pure and Mn doped CeO_2 thin films. In this work, pure and Mn doped CeO_2 thin films have been deposited by employing home-built spray-pyrolysis technique. Employing spray pyrolysis offers advantage of larger deposition area, easy manipulation of various spray parameters and controllability of the composition apart from being more economical and hence adopted in our study.

MATERIALS AND METHODS

Thin films of CeO_2 were deposited using home built spray pyrolysis unit (Jeyaprakash *et al*., 2011) from aqueous solution of cerium nitrate ($Ce(NO_3)_3.6H_2O$) precursor salt obtained from Sigma Aldrich. The solution

Corresponding Author: B.G. Jeyaprakash, School of Electrical and Electronics Engineering, Centre for Nanotechnology and Advanced Biomaterials, SASTRA University, Thanjavur-613 041, Tamil Nadu, India

was prepared by taking 0.05 M of cerium nitrate hexahydrate and was mixed in 50 mL distilled water. This solution was then sprayed as a fine mist onto the glass substrates which were maintained at a temperature of 350°C. The nozzle to substrate distance was maintained at 45 m and was sprayed at an angle of 45°C. To deposit the doped films, 99.9% pure manganese acetate tetrahydrate ($Mn(CH_3COO)_2.4H_2O$) precursor obtained from Sigma Aldrich was used. Two different solutions with different manganese salt concentration (1 and 4 at. wt. %) was prepared. The films were prepared at 350°C and cooled slowly to room temperature. The thicknesses of the deposited films have been estimated using a Veeco Dektak stylus profilometer and were then subjected to characterization studies. X-ray diffractometer (Model XPERT-PRO) employing Cu-Kα radiation (λ = 1.54056 Å) was employed to analyze the structural behaviour of the thin films. Continuous scanning mode and 2θ varying from 10-90° was set to detect the possible peaks. The AC electrical conductivity of films has been studied by impedance spectroscopy using Solartron 1260. The impedance was obtained for a frequency range from 1 Hz to 1 MHz at different temperatures of 50, 100 and 150°C in atmosphere. The DC variation of resistance with temperature was also studied using four-probe method obtained from SES DFP-03 instrument.

RESULTS AND DISCUSSION

Structural analysis: The thickness of pure and Mn doped CeO_2 films were found to vary between 640 and 560 nm, respectively. Figure 1 shows the X- Ray Diffraction (XRD) profiles of pure and Mn doped ceria thin films. As indicative in the diffractogram, all the films exhibited polycrystalline nature and crystallized in a characteristic fluorite-type lattice indexed according to ICDD [34-394]. The undoped films exhibited (111) and (200) preferential orientation whereas the doped samples showed (111) preferential direction growth. The doped films also did not exhibit any additional peaks which is a clear indication that the Mn ions occupy position within cubic lattice of ceria. Similar behaviour was also reported by Pereira *et al.* (2005).

The effect of Mn doping in CeO_2 thin films was evident by observing the peak position and broadening effects. The peak positions showed a slight variation upon doping. In contrast, an appreciable change in peak broadening was observed. With increase in doping, peak

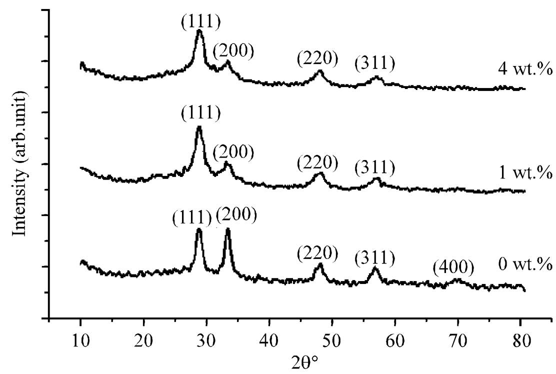

Fig. 1: XRD profile of CeO_2 thin films dropped with various wt.% of Mn

broadening also increased. This shows that the grain size varies upon doping. The grain size was estimated from Scherrer formula. The undoped films exhibited an average grain size of 19 nm. With 1 wt.% Mn doping, the grain size decreased to 16 nm. On further increasing the dopant concentration, the grain size further reduced to 10 nm. The decrease in grain size with increase in dopant concentration shows that the compressional strain in the film increases upon doping. The d-spacing and lattice parameter also showed similar trend. The d-spacing remained constant (3.11 nm) for 1 at. wt.% Mn doping and decreased to 3.09 nm with increase in doping. The lattice parameter decreased from 5.39-5.36 nm upon doping.

AC electrical studies: Impedance analyses of the films were carried out to study the variation of AC conductivity with doping concentration, temperature and frequency. The electrical impedance of CeO_2 thin film was found to increase with increase in dopant concentration. This trend continued irrespective of the increase in temperature. Also with increase in temperature, the electrical resistance was found to increase for all dopant concentrations. This may be attributed due the increase in lattice vibrations which increase with increase in temperature. From the impedance analysis data, it was also found that the impedance of the films decreases drastically with increase in frequency. This clearly indicates that the electrical conductivity decreases at higher frequencies. Figure 2-4 show the variation of the electrical impedance (Z) for different dopant concentration.

DC electrical studies: Figure 5 shows the variation of electrical resistance with temperature for pure CeO_2

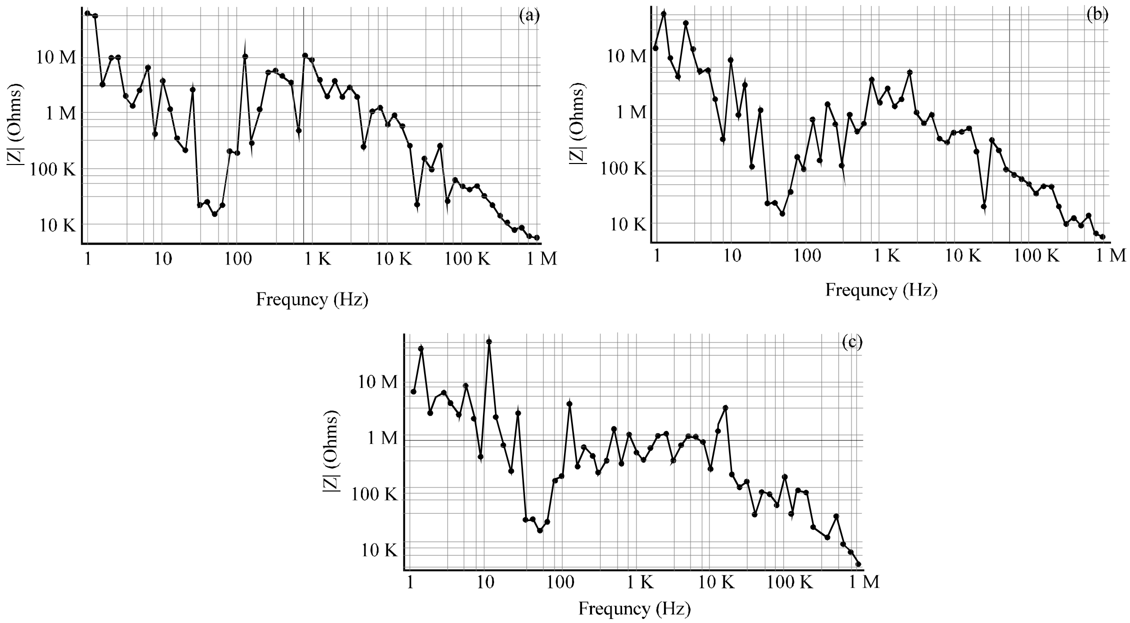

Fig. 2(a-c): Variation of Impedance with frequency of pure CeO_2 thin films at, (a) 50°C, (b) 100°C and (c) 150°C

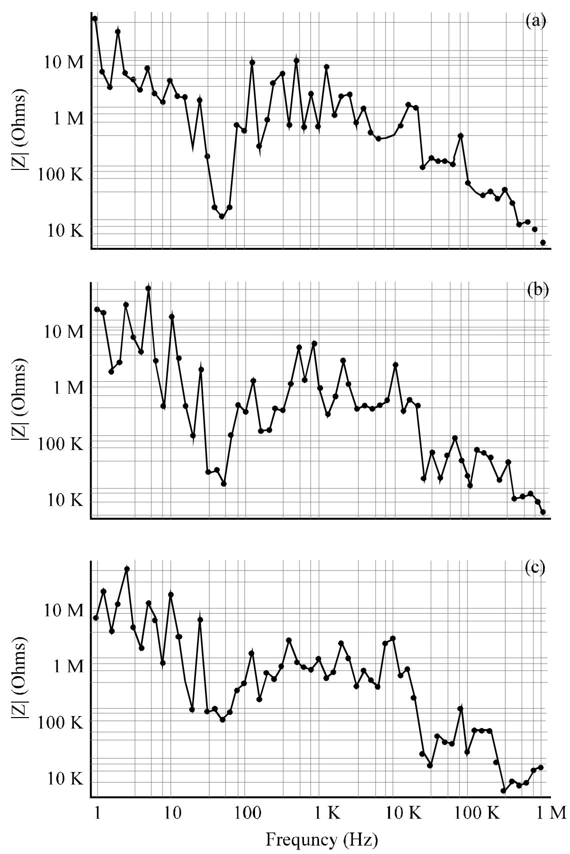

Fig. 3(a-c): Variation of Impedance with frequency of 1 wt.% Mn doped CeO_2 thin films at, (a) 50°C, (b) 100°C and (c) 150°C

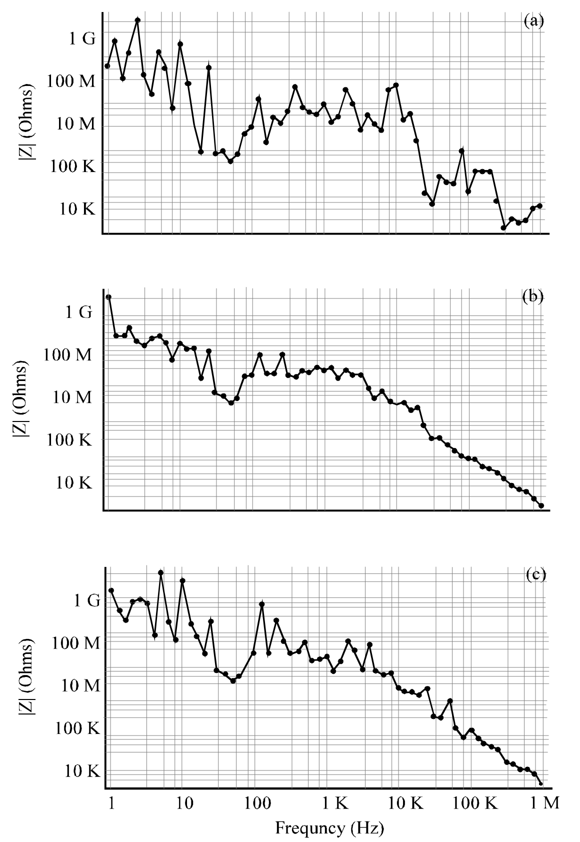

Fig. 4(a-c): Variation of Impedance with frequency of 4 wt.% Mn doped CeO_2 thin films at, (a) 50°C, (b) 100°C and (c) 150°C

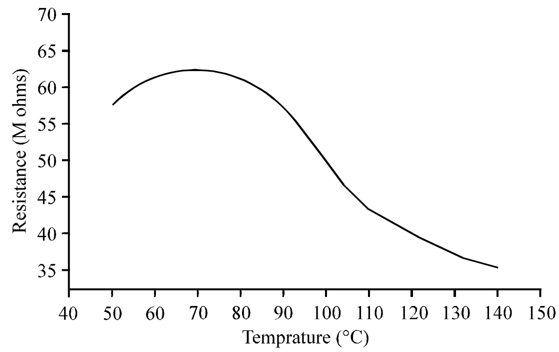

Fig. 5: Variation of electrical resistance with temperature for CeO_2 film

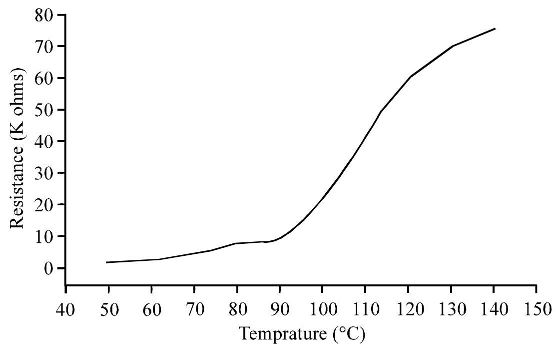

Fig. 6: Variation of electrical resistance with temperature for 4 wt.% Mn doped CeO_2 film

obtained using four probe techniques. The plot clearly indicates that the resistance of the thin film decreases with increase in temperature. This shows that pure CeO_2 film exhibits semiconducting nature. However, when impurity was introduced, there was change from semiconducting to metallic behaviour. The resistance of the film was found to increase with increase in temperature. This is shown by the Fig. 6.

CONCLUSION

In this study, thin films of pure and Mn doped CeO_2 were deposited using home built spray pyrolysis unit. The thickness of the films was found to decrease upon doping. XRD profile indicated that all the films crystallize in fluorite cubic structure. The grain size decreased with increase in dopant concentration. Electrical impedance and resistance of the films also varied drastically upon doping. These drastic changes in the film properties can be well exploited in chemiresistor baser chemical sensing applications.

REFERENCES

De Souza, J., A.G.P. da Silva and H.R. Paes, 2007. Synthesis and characterization of CeO_2 thin films deposited by spray pyrolysis. J. Mater. Sci., 18: 951-956.

Debnath, S., M.R. Islam and M.S.R. Khan, 2007. Optical properties of CeO_2 thin films. Bull. Mater. Sci., 30: 315-319.

Elidrissi, B., M. Addou, M. Regragui, C. Monty, A. Bougrine and A. Kachouane, 2000. Structural and optical properties of CeO_2 thin films prepared by spray pyrolysis. Thin Solid Films, 379: 23-27.

Gupta, S., S.V.N.T. Kuchibhatla, M.H. Engelhard, V. Shutthanandan and P. Nachimuthu *et al*., 2009. Influence of Samaria doping on the resistance of ceria thin films and its implications to the planar oxygen sensing devices. Sens. Actuators B, 139: 380-386.

Jeyaprakash, B.G., K. Kesavan, R. Ashok kumar, S. Mohan and A. Amalarani, 2011. Temperature dependent grain-size and microstrain of CdO thin films prepared by spray pyrolysis method. Bull. Mater. Sci., 34: 601-605.

Konstantinov, K., I. Stambolova, P. Peshev, B. Darriet and S. Vassilev, 2000. Preparation of ceria films by spray pyrolysis method. Int. J. Inorg. Mater., 2: 277-280.

Pereira, G.J., R.H.R. Castro, D.Z. de Florio, E.N.S. Muccillo and D. Gouvea, 2005. Densification and electrical conductivity of fast fired manganese-doped ceria ceramics. Mater. Lett., 59: 1195-1199.

Shenai, K., R.S. Scott and B.J. Balinga, 1989. Optimum semiconductors for high power electronics. IEEE Trans. Electr. Devices, 36: 1811-1823.

Takamura, H., J. Kobayashi, N. Takahashi and M. Okada, 2009. Electrical conductivity of ceria nanoparticles under high pressure. J. Electroceram., 22: 24-32.

Tang, M., Y. Zhou, X. Zheng, Q. Wei, C. Cheng, Z. Ye and Z. Hu, 2007. Microstructure and electrical properties of CeO_2 ultra-thin films for MFIS FeRAM applications. Trans. Nonferrous Met. Soc. China, 17: 741-746.

Wang, S., W. Wang, Q. Liu, M. Zhang and Y. Qian, 2000. Preparation and characterization of cerium (IV) oxide thin films by spray pyrolysis method. Solid State Ionics, 133: 211-215.

Wu, X., Q. Liang and D. Weng, 2006. Effect of manganese doping on oxygen storage capacity of ceria-zirconia mixed oxides. J. Rare Earths, 24: 549-553.