Influence of Mn Doping on Physical Properties of Nanostructured CeO$_2$ Thin Films

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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 it 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$_2$O) precursor salt obtained from Sigma Aldrich. The solution
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(CH₃COO)₂·4H₂O) 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 20 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 CeO₂ 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 CeO₂ 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 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 at. 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 CeO₂ 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 CeO₂,
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
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 based chemical sensing applications.

**REFERENCES**


