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Defect induced magnetic transition in Co doped CeO_2 sputtered thin films

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ABSTRACT

Cobalt-doped cerium dioxide thin films exhibit room temperature ferromagnetism due to high oxygen mobility in doped CeO_2 lattice. CeO_2 is an excellent doping matrix as there is a possibility of it losing oxygen while retaining its structure. This leads to increased oxygen mobility within the fluorite CeO_2 lattice, leading to formation of Ce^{3+} and Ce^{4+} species. Magnetic ceria materials are important in several applications from magnetic data storage devices to magnetically recoverable catalysts. In this paper, the room temperature ferromagnetism of rf sputtered Co doped CeO_2 thin films is reported whereas undoped CeO_2 thin films exhibit paramagnetic behavior. The ferromagnetic properties of the Co doped films were explained based on oxygen vacancies created by Co ions in Ce sites. This is further supported by X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and Raman. Change in surface morphology due to Co doping of the samples were analyzed using atomic force microscopy (AFM).

1. Introduction

In recent years, cerium oxide (ceria) has been the subject of intense work in two different areas of condensed matter research with the driving force being possible technological applications. The key role played by ceria in catalytic applications is well known and hence it is of utmost importance to study its capability for oxygen storage as well as the possibility of reversible oxygen release [1]. On the other hand, the search and development of novel materials that are ferromagnetic beyond room temperature is also currently being explored for spintronics applications [2–5]. In this context, ceria with diluted magnetic impurities becomes a natural candidate, due to its good usability with current electronic devices. However, this material still poses several questions, the main one being the need to find a widely acceptable explanation for the observed room temperature ferromagnetism (RTFM) [6]. The physical origin of this RTFM is currently a subject of controversy and debate, but there seems to be a consensus that oxygen vacancies play a determining role. It is clear that a complete understanding of the physics involved when oxygen vacancies are created is important for both catalysis and spintronics applications.

Several techniques are available for deposition of CeO_2 thin films such as: chemical solution technique [7], spray pyrolysis [8], solution derived method [9], atomic layer deposition [10], rf sputtering [11–13], sol-gel [14], pulsed laser deposition [15], etc., Among these available techniques, rf sputtering is the major industrial process due to its remarkable applications in various fields. Sputtering is used in the semiconductor industry to deposit thin films of various materials for integrated circuit processing. On the other hand, thin antireflection coating on glasses for optical applications is also deposited by sputtering. Because of the low substrate temperatures used, sputtering is an ideal method to deposit contact metals for thin film transistors. Sputtering is also used to deposit the metal layer during fabrication of CDs and DVDs. Sputtering method yields high deposition rate, high volume, and large area uniform thin films on various substrates.

In the present work, $Ce_{1-x}Co_xO_2$ (x=0, 5, 10% and 15%) thin films were deposited by using rf magnetron sputtering technique. The effect of cobalt doping on the structural, surface morphological, optical, compositional and magnetic performance of the thin films were systematically investigated.

2. Experimental procedure

Pure and cobalt doped CeO_2 thin films were deposited by using RF-sputtering (Hind Hivac, Planar Magnetron RF/DC Sputtering Unit Model-12′ MSPT, India) onto glass substrates. The substrates were chemically cleaned well by using chromic acid and acetone. The cleaned substrates were then loaded into the deposition chamber. 5 cm diameter and 5 mm thickness of target was prepared using the commercially available CeO_2 and cobalt powders (Sigma Aldrich and SD Fine Chemicals, respectively). These powders were mixed at various weight percentages (0, 5, 10% and 15% of Co) and then

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compacted to pellets separately with the help of stainless steel pelletizer and hydraulic press. Then, the prepared target was sintered at 1000 °C for 12 h using box furnace (Model: VB Ceramic Consultant, India.). The sintered target was loaded into the chamber and the chamber was evacuated to a base pressure of $\sim 9\times10^{-5}$ mbar. The coating parameters such as target to substrate distance, working pressure, rf power and coating time for the deposition of CeO_2 were set as 6 cm, 3×10^{-3} mbar, 200 W and 30 min, respectively. Substrate temperature was fixed as 200 °C during the deposition of thin films.

Structural properties of thin films were studied by using X-ray diffraction (XRD) with Cu-Kα (λ=0.154 nm) radiation source (X' pert Pro PANalytical) over a 2θ scan range of 10–70°. XPS analysis was carried out using XPS instrument (Carl Zeiss) and all the spectra were recorded under ultra high vacuum with Al Kα line (1486.6 eV) radiation. Surface morphology of the film was studied by using an Atomic Force Microscope (SPM 600, Agilent Technologies). Room temperature photoluminescence (RTPL) study was performed by using Varian Cary Eclipse fluorescence spectrophotometer. Raman spectra of the films were recorded using a micro Raman spectrometer (Acton SpectraPro 2500i, Princeton Instruments, Acton Optics and Coatings). Magnetic properties of the films were performed by using Vibrating Sample Magnetometer (Lake Shore, Model: 7404).

2.1. X-ray diffraction studies

X-ray diffraction patterns of the cerium oxide (CeO_2) and Co doped cerium oxide (Co-CeO_2) thin films are shown in Fig. 1(a). The pattern corresponds to CeO_2 [JCPDS card no. 34-0394] exhibiting a face centered cubic crystalline structure. The patterns of the cobalt doped $Ce_{1-x}Co_xO_2$ (where x=0, 5, 10, 15 wt%) show the formation of Co-CeO_2 thin films. Peak appeared at ~46° correspond to (2 2 0) plane of the CeO_2.

Presence of single peak along (2 2 0) plane indicates that the films tend to grow in the perpendicular direction to the substrate. There are no peaks corresponding to CoO, Co_3O_4 or Co_2O_3, confirming the fact that only Co ions are incorporated into CeO_2. When Co ion concentration is increased, a slight shift in (2 2 0) peak position to the lower angle is observed. This shift confirmed about the substitution of the Co ions in Ce sites. The lattice parameter and the crystallite size values were determined and are shown in Fig. 1b. Both parameters increased as the Co ion concentration increased up to 10 wt% and then started to decrease at the concentration of 15 wt%. The same phenomenon was observed by Mahmoud et al. [16] and the changes may be explained as follows: the incorporation of the smaller Co^{2+} ions (0.058 nm) into the Ce^{4+} ion sites cause in the reduction of the Ce^{4+} ions (0.09 nm) to the Ce^{3+} ions (0.101 nm) to accommodate the change in size and the corresponding increase of the lattice constant as well as the crystallite size up to the 10 wt% Co concentration. When there is further increase above this critical concentration, the Co^{2+} ions (0.058 nm) tend to oxidize to Co^{3+} ions (0.047 nm) which result in a decrease of the lattice constant and the crystallite size [17]. The reduction of dislocation density and strain with respect to different Co concentrations up to 10 wt% is presented in Fig. 1c.

2.2. XPS spectra analysis

The combination and oxidation states of Co-CeO_2 thin films were examined by XPS analysis. The XPS spectra of wide, Ce 3d, O 1s and Co 2p core levels of prepared thin films were recorded and are shown in Fig. 2a–f. Fig. 2a depicts the wide spectra for pure and Co-CeO_2 thin films. Binding energy values of C 1s, O 1s, Ce 3d and Co 2p peaks were observed from these wide spectra. Ce 3d core level spectra are presented in Fig. 2b. Generally, the Ce 3d spectra is known to be complicated due to the existence of two different oxidation states and the hybridization of O 2p valance band with

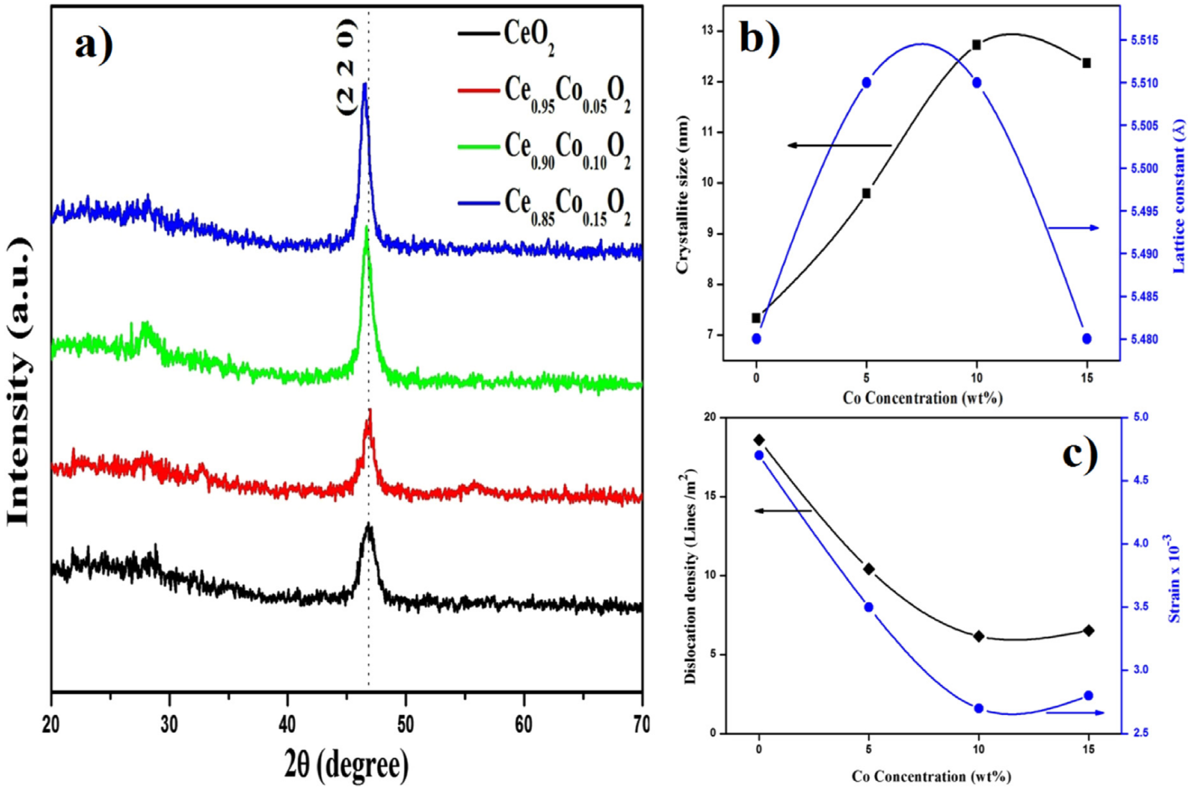

Fig. 1. a) XRD patterns of different wt% of Co doped CeO_2 thin films (Co=0, 5, 10 and 15%), b) Change in crystallite size and lattice constant with respect to the Co concentration (Co=0, 5, 10 and 15%), c) Change in dislocation density and strain with respect to the Co concentration (Co=0, 5, 10 and 15%).