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Influence of Co concentration on the structural, optical, morphological and photo-diode properties of cerium oxide thin films

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ABSTRACT

Highly uniform and well-dispersed ring shaped particles of CDC (Cobalt doped cerium oxide) films are successfully deposited by Nebulizer Spray Pyrolysis (NSP) technique. The structural, morphological, optical and photo-diode properties of the films are investigated. Cubic fluorite crystallites are detected by X-ray diffraction pattern with preferred orientation along (111) direction. Co concentrations distress the crystallinity and structural parameters. The transmittance decreases with increasing Co concentration due to the presence of covalent bonds between cerium and oxygen. PL spectra revealed that three consistent sharp and broad peaks observed at 369 (3.31 eV), 394 (3.14 eV) and 425 nm (2.91 eV) correspond to near-band-edge emission (NBE) in UV region, deep level emission (DLE) in violet and blue of the visible region respectively. The deep level emissions result from the recombination of electrons with holes trapped in singly ionized oxygen vacancies (Vo+). Large agglomerated ring, button and spherical crystallites are obtained with the typical size in the range 83–207 nm. XPS analysis exhibits the presence of Ce, Co, O, C and Na in the films that indicates the non-stoichiometric behavior. I-V characteristics show the rectifying nature with a typical forward to reverse current ratio of ~7 in the range −4 to +4 V. The turn-on voltage of the hetero-junction is found to be ~1.7 V. The transient photocurrent behavior indicates that the device has a good stability and quick response to suggests that the prepared hetero-junction device can be used as a white light photodetector and UV detector applications.

1. Introduction

Transparent semiconducting oxide thin films are fascinating due to their good optical characteristics, high stability and excellent electrical properties. Transparent conducting oxides are basically metal oxide semiconductors that can be classified as either n-type or p-type. Currently, transparent conducting n-type semiconductors are required in a variety of optoelectronics applications. In particular, CeO_2, the most exhaustively investigated n-type transition rare earth metal oxide, is a pertinent candidate for many applications like cathode materials in batteries [1], solar thermal absorbers [2], electrochromic display devices [3–5], heterojunction solar cells [6] and gas sensing applications [7–9]. CeO_2 is a wide band gap, low cost, promising ion storage material in terms of cyclic stability [10]. In recent years several studies have been carried out to modify the properties of CeO_2 thin films by doping with various elements like Cu^{1+}, Ru^{3+}, Al^{3+}, Co^{2+}, In^{3+}, Mn^{3+}, Y^{4+} and Gd^{3+} [10,11–15]. Among these, cobalt oxide is a very pleasant material due to its numerous applications and uses in the domain of various technological fields [16]. Cobalt may exist in both Co^{2+} as well as Co^{3+} oxidation state depending on the sites occupied by cation in the host lattice [17].

In our previous works, the effect of deposition parameters and doping concentration on the nanostructured ceria films could be investigated and reported [18–23]. There are some reports on the spray deposition of cobalt doped ceria [24,25]. Very few studies have been reported on the deposition of nanosized ceria films to fabricate p-n junction diode [26,27]. Attempts have been made to prepare cobalt doped ceria thin films and investigate their structural, optical, electrical and rectification properties. This paper presents the feasibility study on the rectification properties of spray coated CDC thin films.

2. Experimental details

The spray solution is prepared by dissolving 0.08 M cerium nitrate in 20 ml of de-ionized water and ultrasonicated for 10 min and the obtained solution is continuously stirred for 20 min using

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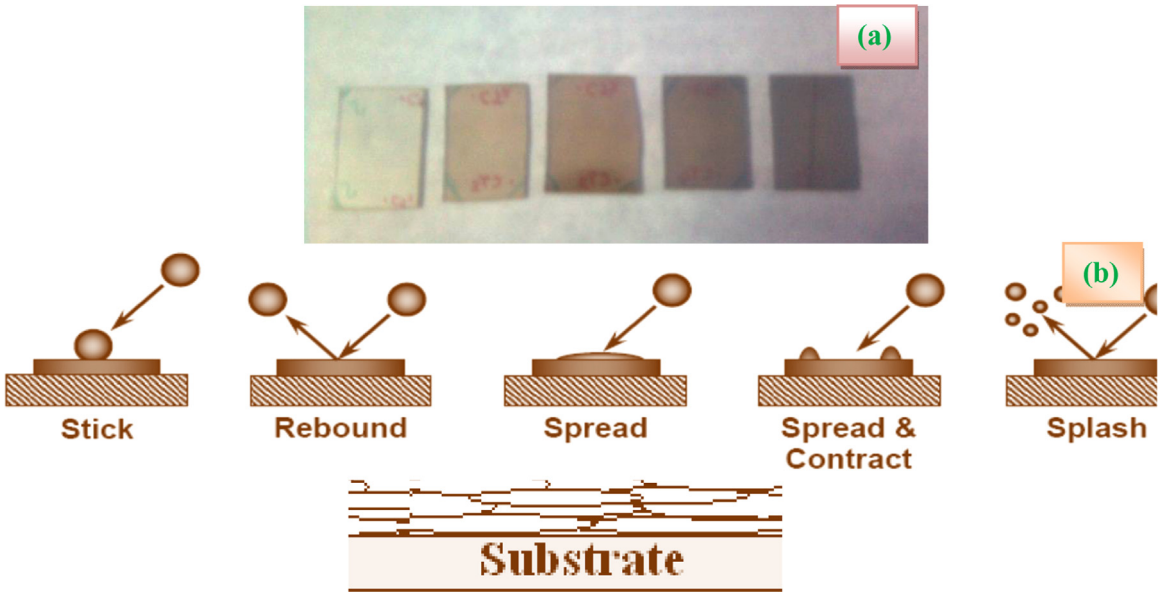

Fig. 1. (a) Photograph of the prepared Cobalt Doped Cerium oxide (CDC) thin films. (b) Possibility of spray droplets landing on the substrates.

magnetic stirrer. Similarly, cobalt (II) nitrate solution is prepared with 5%, 10%, 15%, 20% and 25% (wt%) of 0.08 M cerium nitrate. The stirring is continued for 30 min to get clear and homogeneous spray solution. The prepared solution is sprayed through the nebulizer, which is connected to an air compressor maintained at a constant pressure 40 Psi onto the ultrasonically cleaned glass substrates kept at 400 °C (controlled within ±5 °C). The films prepared by this method (Fig. 1(a)) have good adherence to the substrates with smooth surface.

Several complementary methods are used to characterize the properties of the obtained samples. The vibrational measurements are carried out at room temperature using the normal KBr disc technique. IR spectra are taken with a BrukerIFSTable 88 spectrometer in the range 4000–400 cm^{-1}. The samples are characterized for their purity and crystallinity by X-ray powder diffraction (XRD) using XPERT-PRO, Bruker AXS D8 Advance X-ray diffractometer. Surface morphology of the samples are analyzed by Scanning electron microscopy (SEM) and Atomic force microscopy (AFM) using JEOL Model JSM – 6390LV instrument for high resolution surface imaging and Nanosurf easyScan2 for measuring surface roughness respectively. Commercially available AFM tips (detector side Al coating, the thickness of the tip is 7 mm, tip length is 225 mm, tip width is 38 mm with a 48 N/m force constant and 190 kHz resonant frequency) are used in intermittent contact mode for the above analysis. I-V Characteristics are analyzed with the help of Keithley electrometer 6517B.

3. Results and discussion

3.1. Structural properties

Fig. 2 shows the XRD patterns CDC thin films deposited at an optimized substrate temperature (Ts) 400 °C. Some of the Ce^{4+} cations are easily substituted by Co^{2+} cations without any lattice distortion due to the atomic size similarity (Ionic radii of Ce and Co atoms are Ce=0.97 Å and Co=0.65 Å respectively) in the CDC films. At lower Co concentration (5%), the nearly amorphous nature is confirmed with the presence of single peak at 2θ=28.8. It also shows a small hump at the diffraction angle 20–25° due to the amorphous glass substrates and formation of low thickness. At higher Co concentration, the crystalline nature of cubic fluorite

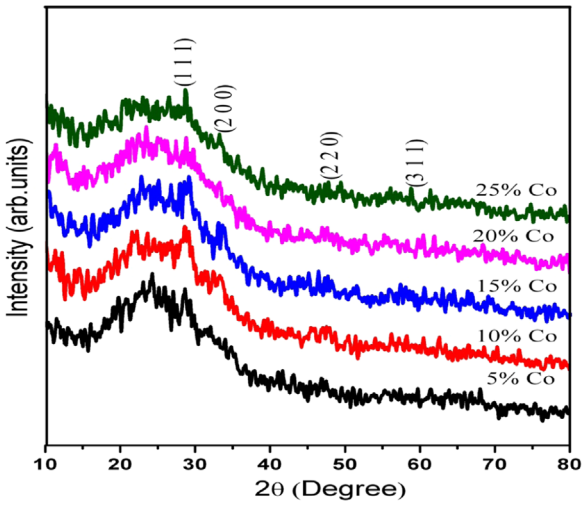

Fig. 2. XRD Patterns of spray coated CDC films.

structure with preferred orientation along (1 1 1) direction is confirmed [28]. The additional peaks are observed at 2θ=33.54, 47.12, 56.35 and 69.31 due to the (2 0 0), (2 2 0), (3 1 1) and (4 0 0) hkl planes respectively. Incorporation of Co^{2+} ions into the Ce^{3+} lattice distorts the arrangement of crystallites and reduces the crystalline nature of pure cerium oxide. The crystallite size decreases with increase in higher dopant concentration of Co. Basically, the addition of a dopant into a crystalline structure affects the crystalline growth kinetics [11]. It is observed that the lattice constant is found to be varied from 5.3799 to 5.4614 Å with the increase of Co concentrations from 5% to 25%. The average crystallite size is found to increased with the increase of Co concentration upto 15% and then decreases may be due to the supersaturation of atoms. This poor crystallinity may ascribe to the amount of solute reaching the surface of the substrate to form film and the larger electrostatic interaction between solute particles. Because of the smaller size of the dopants, there should be considerable decrease in the lattice parameter of the CeO_2 lattice.

Fig. 3 shows the FT-IR spectra of CDC thin films prepared with different Co concentrations. The broad absorption band located at 3517 cm^{-1} corresponds to O-H stretching vibration of residual water and hydroxyl groups, while the absorption band at