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A Comparative Study of Structural and Morphological Properties of Pristine and Mn Doped Ruthenium Oxide Thin Films

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Abstract: Mn-doped and pristine Ruthenium Oxide composite nanostructures in thin film form were prepared on stainless steel substrates by sol-gel spin coating method. The at % of Mn was increased as 0.1, 0.2, 0.5, 1 and 2 %. The X-ray diffraction study showed crystalline behaviour for both pristine and doped films with porous morphology. The variation in lattice constants for both RuO_2 and MnO_2 was observed with increase in doping percentage. EDAX spectrum showed the successful doping of Mn in RuO_2. The infrared spectrum of as deposited pristine RuO_2 thin film depicted strong absorption bands at 880.41 cm^{-1} and 749.52 cm^{-1} indicating the stretching mode of Ru=O and O-Ru-O respectively. The absorption peaks attributed to the –OH bending vibrations along with Mn atoms were also seen.

Keywords: Pristine RuO_2, Mn doped RuO_2, XRD, SEM, FTIR, EDAX.

1 Introduction

Low resistivity, good thermal stability, high resistance to chemical corrosion , these desirable characteristic have attracted Ruthenium Oxide for its diverse applications in various fields [1-6]. It is well known that the capacitance of RuO_2 electrode results from redox pseudocapacitance. However, the current response resembles an ideal capacitor, which is a ‘‘rectangular’’ shape under cyclic voltammetry. It has been widely used in supercapacitor because of its good catalytic properties [7].

Even though RuO_2 has a great advantage in terms of a wide potential range of highly reversible redox reactions with high specific capacitance, it is expensive. Therefore, it is desirable to develop a process for the preparation of thin film RuO_2 electrodes to reduce their cost as capacitor electrodes [8].

Another metal oxide Manganese oxide is of considerable importance in technological applications due to its natural abundance coupled with environmental compatibility and also intensively investigated as promising electrode material in electrochemical capacitors [9-11]. In the current work, thin films of pristine Ruthenium oxide and Mn doped Ruthenium oxide were preferred as the form of the samples to be synthesized because the controlled synthesis of materials as thin films is a elementary step in many applications.

2 Experimental

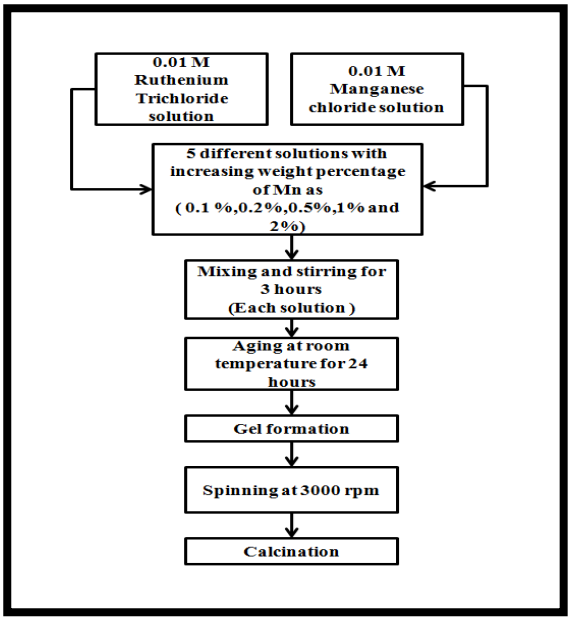

Figure 1. Flow chart of thin film preparation by the sol–gel spin coat route.

Here attempts are made for the synthesis of pristine RuO_2 and Mn doped RuO_2 thin films so as to minimize the quantity of Ruthenium material and to achieve the required results. For this, sol-gel spin coating deposition technique was used which allows the uniform deposition of the gel on the substrate. Also the structural, morphological and

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electrochemical properties in terms of XRD, SEM, EDAX, and FTIR were studied with increasing doping percentage of Mn in RuO_2. For doped samples, Ruthenium trichloride and Manganese trichloride solution of molarity 0.01 M each were prepared. Then doping percentage of Mn was increased as at 0.1 %, 0.2%, 0.5%, 1% and 2%. After stirring and setting for 24 hours gel was formed. Then the gel was deposited on properly cleaned SS substrates in spin coater unit. After annealing, uniform and thin films were obtained. Figure 1. shows the flow chart of doped thin film preparation.

3 Results and Discussions

3.1 Structural Properties

The structures of thin films were analysed by X-ray diffraction with a diffractometer Rigaku Ultima IV, Japan using CuKα radiation (λ= 1.54 A°) by varying diffraction angle 2θ from 10° to 80°. The X-ray diffraction pattern of as deposited pristine RuO_2 and Mn doped RuO_2 thin films thin films are shown in Fig.2.

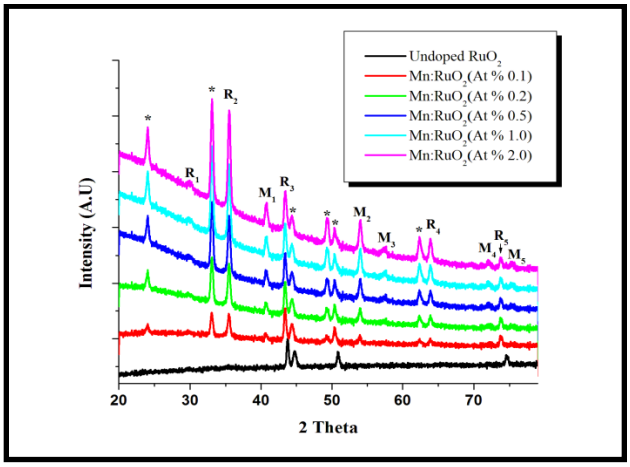
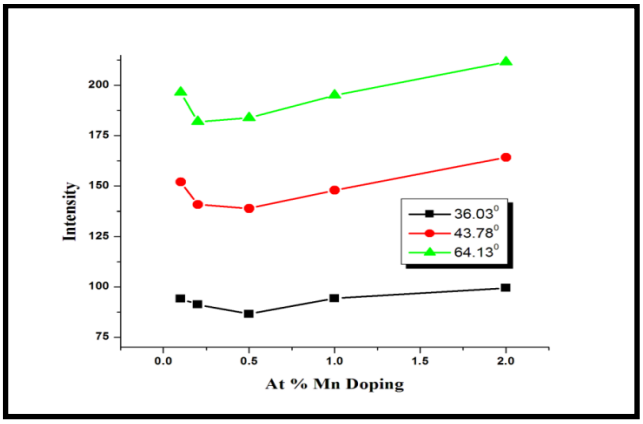
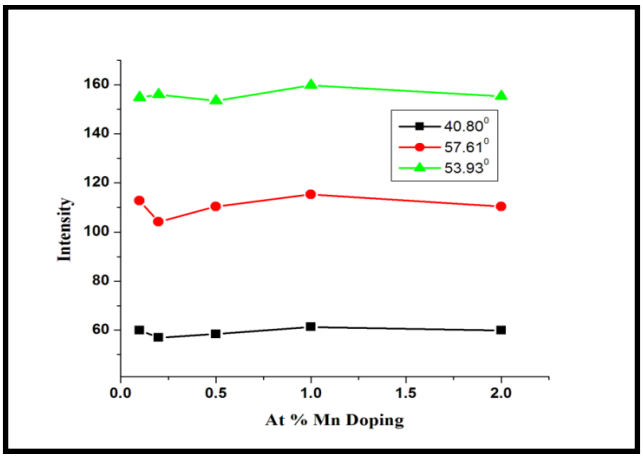


Figure 2. XRD of pristine and Mn doped RuO_2 thin films.

The experimental data showed the crystalline nature of RuO_2 with tetragonal structure having lattice constants of a = b = 4.5834 A°, c = 3.0875A° with d = 2.99,2.53,2.08,1.46 and 1.28 A° corresponding to Miller Indices [110], [101], [210], [310], and [202] respectively which are in good agreement with JCPDS card (JCPDS Card No.-88-0322). Similarly orthorhombic structure of MnO_2 with lattice constants a= 9.2322 A°, b = 4.4400 A° and c = 2.9182 A° with d = 2.22, 1.60, 1.49, 1.32 and 1.26 A° corresponding to Miller indices [020] , [420], [511], [031] and [231] respectively which are also in good agreement with JCPDS card (JCPDS Card No.-82-2169). The peaks which are labelled as **"*"** correspond to stainless steel. It was observed from XRD that there is a shift in 2 theta to lower values for every observed dominant peak of RuO_2 and also the intensity of corresponding peaks has been decreased with increasing doping concentration of Mn. The variation in intensity for dominant peaks of RuO_2 and MnO_2 on increase in at % Mn doping concentration is shown in figure 3.



[a]



[b]

Figure 3. Intensity variation for (a) RuO_2 and (b) MnO_2 peaks at dominant peaks with increasing at % doping of Mn.

Usually on doping, the peak intensity decreases which might be due the change in electron density or might be due to point defects. Intensity change is related to adsorption on surface while change in theta indicates inter-layer change. **S**hift of Bragg peaks to lower values of the diffraction angle, increases lattice parameter and shift of Bragg peaks to higher values decreases lattice parameter as shown in table 1.The variations in lattice constants are given in table 1.

Table 1. Increase in lattice parameters of RuO_2 due to increase in doping percentage of Mn

	RuO_2	
	a = b	c
Undoped RuO_2 thin films	4.52 A°	3.12 A°
Mn doped RuO_2 thin films	4.58 A°	3.08 A°

3.2 Morphological Properties

The two-dimensional surface morphological study of thin films has been carried out from SEM image . The surface morphology was analyzed by scanning electron microscopy (SEM JEOL JSM 6360). Figure 4. shows the SEM image pristine RuO_2 thin film. The SEM image showed non-uniformly distributed aggregates giving rise to a high surface roughness. Such porous and "mud-cracked" morphology is favourable for penetration of electrolyte.

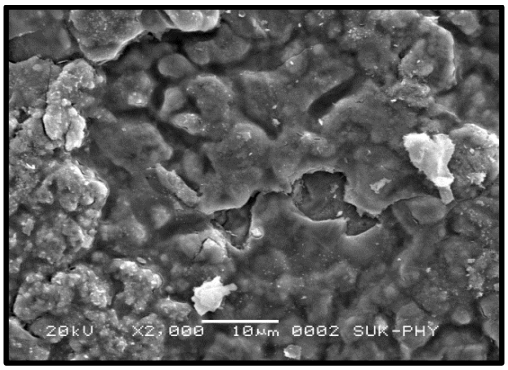


Figure 4. Surface Morphology of pristine RuO_2 thin film.

The surface morphological images of Mn doped RuO_2 thin films with increasing doping concentration of Mn for higher magnification are depicted in figure 5.

The morphology showed that the substrate is well covered with RuO_2 material. The porous structure created due to the interconnected structure can also be clearly seen. It is evident from SEM images that the various randomly distributed interconnected macropores are present over the substrate. It is clearly seen that the number of pores and their size was increased with doping concentration from 0.1 to 1 at % Mn doping. But for 2 at % of Mn doping the number of pores and their size was changed considerably.

Sufficient void spaces in and between the pores, pore size distribution and such porous structure greatly assist the ion diffusion from the electrolyte into the electrode, which raise the specific capacitance. Admirable electrochemical performance as an electrode for a supercapacitor could be demonstrated due to the interconnected structure [12].

EDX is a characterisation technique that provides elemental composition of various constituent elements in a material. The abscissa of the EDX spectrum indicates the ionization energy and ordinate indicates the counts. The compositional analysis of the as deposited thin films was carried out using EDAX technique by Quanta 200 ESEM instrument.

Higher the counts of a particular element, higher will be its presence at that point or area of interest. The elements of deposits on the top of SS , pristine $RuO_2$and Mn doped RuO_2 were studied using EDX spectrums. The presence of Ni, Fe, Cr belongs to SS (fig.6. a) and the presence of elements such as Ru and O is assigned to the formation of RuO_2 (fig.6 b) . Mn incorporated in (fig. 6. c) RuO_2 shows successful doping. There was increment in the weight percentage of Mn with increase in doping percentage.

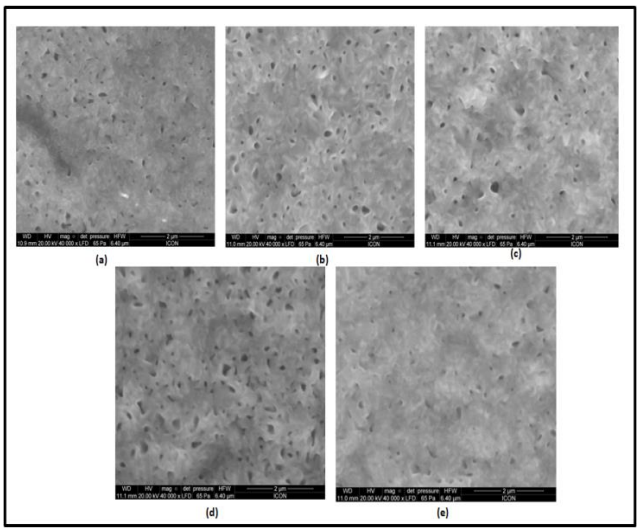


Figure 5. SEM images for Mn doped RuO_2 samples (a) 0.1 at % (b) 0.2 at% (c) 0.5 at% (d) 1 at% (e) 2 at%.

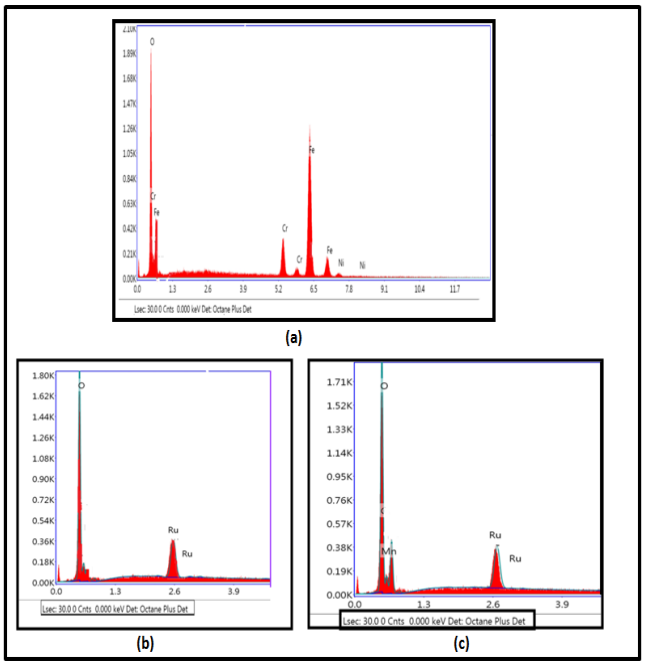


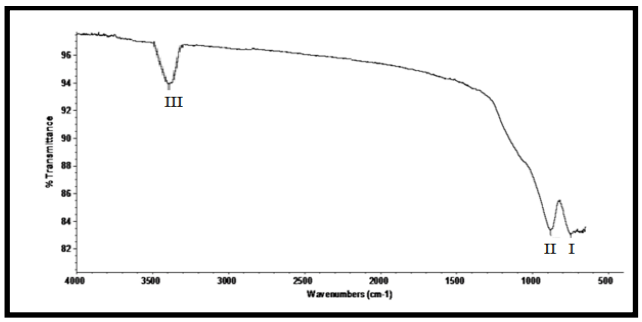
Figure 6. EDX Spectrum : a) Empty SS b) pristine RuO_2 c) Mn doped RuO_2

3.3 FTIR Spectroscopy

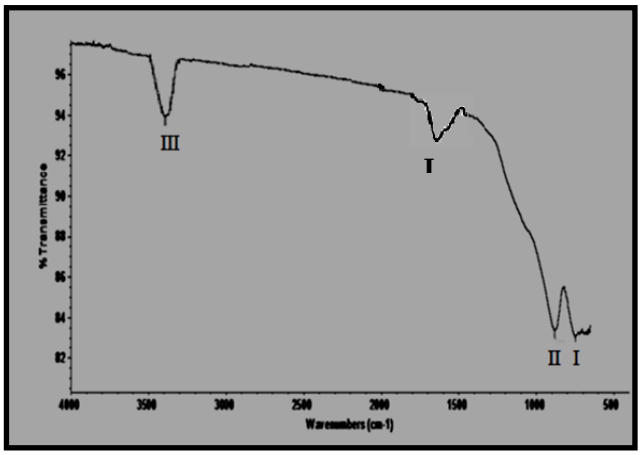
For study of surface features of materials and for the examination of absorbed molecules on a solid surface, Fourier Transform infrared spectroscopy is a well known technique.IR spectroscopy was used to obtain additional information on the phases as well as structure transformations of RuO_2 and MnO_2 phases.

Figure 7. describes the dependence of optical spectra in the range 500 cm^{-1} to 4000 cm^{-1} for Ruthenium Oxide thin

films. The infrared spectrum of as deposited pristine RuO_2 thin film depicts strong absorption bands at 880.41(II) cm-1 and 749.52 (I) cm-1 indicating the stretching mode of Ru = O and O – Ru - O [13]. The absorption band at 3410 cm^{-1} (III) is attributed to the stretching vibration stretching vibrations of OH-. This result indicated that, as deposited film contained hydroxide and other bonds, which indicates that formation of hydrous ruthenium oxide that may play important role in capacitive behavior [14]. The absorption peaks around 1650 cm^{-1} may be attributed to the –OH bending vibrations along with Mn atoms [15].



[a]



[b]

Figure 7. FTIR Spectrum of [a] pristine RuO_2 and [b] Mn : RuO_2 Thin Film.

4. Conclusion

From the above results it can be concluded that Sol-gel spin coating technique can be used as an efficient and cheap method for the synthesis of pristine and Mn doped ruthenium oxide thin films. It showed the admirable variations in structural and morphological properties with increase in Mn at % doping. There is an increase in lattice constants with doping. EDAX spectrum showed the successful doping of Mn in RuO_2.The infrared spectrum of as deposited pristine RuO_2 thin film depicted strong absorption bands at 880.41 cm^{-1} and 749.52 cm^{-1} indicating the stretching mode of Ru=O and O-Ru-O respectively. The absorption peaks attributed to the –OH bending vibrations along with Mn atoms are also seen.

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