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Electrochemical supercapacitive performance of spray deposited Co_3O_4 thin film nanostructures

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ABSTRACT

In this report, we have obtained cobalt oxide (Co_3O_4) nanostructures at various substrate temperatures by chemical spray pyrolysis using mixed aqueous/organic solvent. The influence of substrate temperature on the film properties has been studied. From X-ray diffraction studies the cubic phase of Co_3O_4 is confirmed. SEM shows porous morphology, which is advantageous for supercapacitor applications. Two direct allowed optical transitions are observed. Co_3O_4 nanostructures exhibit good electrochemical performance with excellent cycle stability and high specific capacitance of 425 Fg^{-1} at a scan rate of 5 mVs^{-1}. Specific capacitance of Co_3O_4 films decayed to 7.44% at 1 Ag^{-1} after 1000 charge/discharge cycling tests in 2 M aqueous KOH electrolyte. The electrochemical impedance spectroscopy study indicates that Co_3O_4 nanostructures deposited at 350 °C substrate temperature has better electrochemical properties. The present study is suitable in developing new class of portable energy storage devices.

1. Introduction

In day to day life, the problems of energy utilization and environmental concerns along with human development are facing challenges. Today, the world's massive energy demands are mainly accomplished by the conventional and environmentally unfavorable fossil fuels. To replace this, pursuit of the renewable and clean energy sources, including hydrogen storage and supercapacitors have become important [1–3]. Supercapacitors have appealed significant attention due to their high power density; fast charge/discharge rate and good cycle stability against galvanostatic charge/discharge [4–9].

A balanced surface area and porous surface are highly desirable for electrode materials to be utilised in electrochemical supercapacitors, which is provided by metal oxides [10]. Out of the various metal oxides, ruthenium oxide is the most favorable electrode material with outstanding specific capacitance but its cost is huge. Cobalt oxide is one of the most studied oxides because of its use in various applications, such as solar selective absorbers, pigment for glasses and ceramics [11] and catalyst for oxygen evolution and reduction reaction [12]. It is also widely used as an electrochromic material, sensors, and electrochemical anodes [13], supercapacitors [14–16]. Cobalt oxide exists in three forms, CoO, Co_2O_3 and Co_3O_4, but Co_3O_4 is excessively reported having large applications due to its strong chemical stability and better electrochemical properties. Co_3O_4 in thin film form can be deposited by employing different deposition techniques such as sputtering [17], hydrothermal [18], coprecipitation [5,19], chemical route [20], chemical vapor deposition [21], sol-gel [22] and spray pyrolysis [23,24]. Amongst these, spray pyrolysis has numerous benefits including low cost, flexibility, ability for depositing porous and nanostructure thin films and appropriate for large area deposition.

Kandalkar and coworkers [20] have prepared cobalt oxide films on a copper substrate at room temperature. These films showed a maximum specific capacitance of 165 Fg^{-1} in 1 M aqueous KOH electrolyte at sweep rate of 10 mVs^{-1}. Amin-Chalhoub et al. [21] have processed low reflective CoO coatings by CVD. A fractal cauliflower like morphology was observed. Ambare and colleagues [23] have studied spray deposited ruthenium incorporated cobalt oxide electrodes. The double-pseudo-capacitive behavior with specific capacitance of 628 Fg^{-1} at the scan rate 1 mVs^{-1} in 1 M KOH has been observed. The spray deposition of cobalt oxide nanowires on stainless steel substrates is also reported in the literature [25]. From these and other [5,12–16] studies, it is well understood that Co_3O_4 is the most beneficial material for the supercapacitor uses. Therefore in current investigation, it was decided to deposit good quality Co_3O_4 nanostructures for

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high-performance supercapacitors by chemical spray pyrolysis using mixed aqueous/organic solvent.

In the current report, the effect of substrate temperature on various physical and electrochemical properties of Co_3O_4 thin films is studied. It is perceived that film thickness increases with increase in substrate temperature reaches maximum at 350 °C and decreases thereafter. XRD study confirmed the cubic phase of Co_3O_4. Porous morphology is seen from SEM. The as deposited Co_3O_4 at 350 °C saw minimum electrical resistivity of 2.08×10^3 Ω cm. The films are highly capacitive with maximum specific capacitance of 425 Fg^{-1} at scan rate of 5 mVs^{-1}. The noteworthy cycle stability of 92.56% has been observed at a current density of 1 Ag^{-1} after 1000 charge/discharge cycles.

2. Experimental

2.1. Deposition of FTO substrates

The 2 M stannic chloride with 20 wt% doping of ammonium fluoride was used for deposition of fluorine doped tin oxide (FTO) glass substrates. For all depositions, 10 cc from stock solution is mixed with 10 cc of propan-2-ol to create the 20 cc final spraying solution. This 20 cc solution is sprayed on preheated substrates at 475 °C. These FTO substrates have the sheet resistance of 8–10 Ωcm^{-2}.

2.2. Deposition of Co_3O_4 thin films

A mixture of 0.05 M cobaltous chloride ($CoCl_2.6H_2O$) in a 1:1 (Propan-2-ol + Water) was used as precursor solution. Thoroughly cleaned amorphous glass microslides supplied by Blue Star Corporation and FTO coated glass were used as substrates. Substrates were retained at 30 cm from tip of the nozzle. The computerized spray pyrolysis technique was in employment for the deposition [26]. The deposition temperature is varied at the interval of 25 °C from 300 °C to 400 °C.

2.3. Characterization of Co_3O_4 thin films

The physical characterization of Co_3O_4 films is performed with X-ray diffractometer (wavelength λ=0.15406 nm for Cu-Kα radiation). The surface of Co_3O_4 is analyzed through JEOL-JSM-6360A analytical scanning electron microscope. Optical band gap of Co_3O_4 thin films is assessed by recording absorption spectra in the wavelength range 350–1100 nm. The electrical study is performed with the help of a DC two-point probe method.

The electrochemical characterization is carried out using electrochemical analyzer supplied by CH Instruments, USA in 2 M aqueous KOH electrolyte. Prior to the electrochemical measurements, the electrodes were immersed in the electrolyte for up to 4 hours in order to eliminate the effect of the electrode preparation and obtain more stable values.

3. Results and discussion

3.1. Film formation

The Co_3O_4 nanostructures were deposited at various substrate temperatures. The as deposited Co_3O_4 thin films appear blackish in color. The possible reaction mechanism can be written as:

$$3CoCl_2 + 2H_2O + O_2 \rightarrow Co_3O_4\downarrow + 3Cl_2\uparrow + 2H_2\uparrow \quad (1)$$

The similar type of reaction was also reported earlier by Shinde and coworkers [24] for Co_3O_4. Film thickness of spray deposited cobalt oxide thin films is computed by gravimetric weight difference method using sensitive precision mass microbalance (LC = 0.01 mg). Fig. 1 shows the plot of film thickness versus substrate temperature. The lower substrate temperature (below 300 °C) is not sufficient to carry out the chemical reaction and results into formation of non-adherent amorphous and powdery films; at lower temperatures the spray droplet hit on the hot substrate removing a lot of heat producing partial decomposition of the starting ingredients. Co_3O_4 thin films synthesized at and above 300 °C are polycrystalline. It is realized that film thickness enhances with rise in substrate temperature from 300 °C to 350 °C, achieves terminal thickness at 350 °C (273 nm), beyond which it drops. This can be described as follows: At 300 °C the temperature may not be adequate to decompose the sprayed droplets of cobalt ions resulting in lower thickness. At 350 °C decomposition takes place at the optimum rate ensuing in terminal thickness being reached. A clear drop in film thickness with rise in substrate temperature is witnessed after 350 °C. This is ascribed to higher evaporation rate of the starting ingredients. Similar type of behavior was earlier reported for spray pyrolyzed SnO_2 thin films [27]. The deposited masses for these films are 0.12 $mgcm^{-2}$, 0.15 $mgcm^{-2}$, 0.17 $mgcm^{-2}$, 0.16 $mgcm^{-2}$ and 0.14 $mgcm^{-2}$ for films deposited at 300 °C, 325 °C, 350 °C, 375 °C and 400 °C respectively.

3.2. Structural analysis

Structural analysis of spray deposited cobalt oxide thin films is accomplished using X-ray diffraction (XRD) with CuK$_\alpha$ radiation in the 2θ range between 10° and 90°. Fig. 2 shows the XRD patterns of Co_3O_4 nanostructures deposited at various substrate temperatures. From figure, it is observed that films are polycrystalline and the diffraction peaks are observed at 2θ angles 19.30°, 31.54°, 37.18°, 45.09°, 59.72° and 65.31° matching with (111), (220), (311), (400), (511) and (440) planes respectively. The comparison of observed and standard 'd' values approve cubic phase of Co_3O_4 with lattice parameters a = b = c = 0.8016 nm, which is marginally less than the standard JCPDS value 0.8084 nm [28]. The XRD shows that the peak (311) intensity grows with rise in substrate temperature up to 350 °C, and then falls thereafter. The diminishing crystallinity after 350 °C might be due to re-evaporation of the material from the film surface and decrease in the film thickness [29]. It has been reported that the preferred orientation of oxide films is influenced by source compound, solvent and growth parameters such as precursor

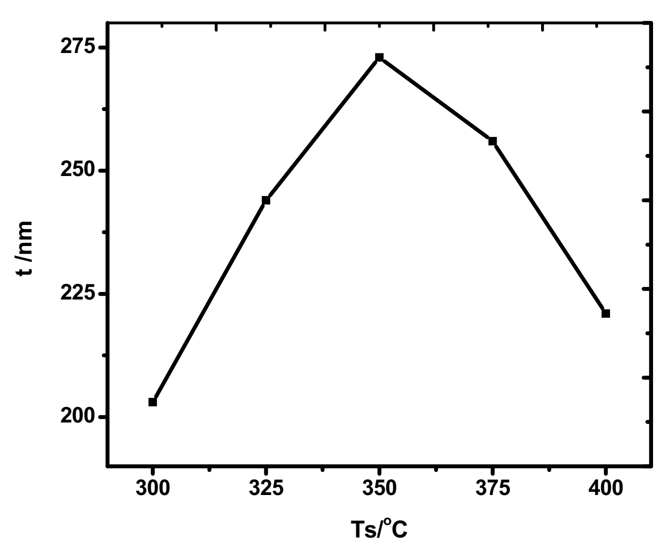

Fig. 1. Variation of film thickness (t) with substrate temperature (Ts) for spray deposited Co_3O_4 thin films.