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Physical and Electrochemical Properties of Molybdenum Doped Nickel Oxide Thin Film Electrodes

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ABSTRACT

In this work, undoped and Mo doped nickel oxide thin films at 2, 4, 6, 8 and 10% Mo doping concentrations have been successfully deposited on glass and fluorine doped tin oxide substrates by chemical spray pyrolysis (CSP) technique at substrate temperature of (370 °C). The effects of Mo dopant on structural and electrochemical properties of NiO thin film have been investigated. X-ray diffraction study shows that transformation of crystal structure from cubic structure in pure NiO to rhombohedral structure in doped NiO with (2 0 2) as preferred orientation wheares (1 1 1) as preferential orientation in pure NiO. X-ray diffraction graph shows that crystallinity of the films decreases with increase in doping concentration. Electrochemical behavior of the deposited films is carried out in 1 M KOH electrolyte using cyclic voltammetry (CV). The maximum specific capacitance 620 Fg^{-1} was found at 2% Mo concentration at 5 mV/s scanning rate which is lower than that of pure NiO.

Keywords: cyclic voltammetry (CV), chemical spray pyrolysis (CSP) technique, NiO, X-ray diffraction.

INTRODUCTION

For clean and efficient energy storage nowadays, more and more attention has been paid to various power source devices such as Li-ion batteries, supercapacitors, fuel cells and so on [1,2]. Among these power source devices supercapacitors are one of the promising power sources and energy storage devices which attracted great research interest because of their efficient energy delivery, high power density and long life cycle [3, 4]. Supercapacitors are classified into electric double layer capacitors (EDLCs) and pseudocapacitors based on the storage mechanism. In particular, transition metal oxides (NiO, MnO_2, RuO_2, Co_3O_4 etc.) are considered as promising electrode materials in pseudocapacitors due their high specific capacitance. Nickel oxide (NiO) is one of promising candidate material for supercapacitors because of its unique characteristics such as high theoretical capacitance, superior reversibility, stability and potential applications in electrodes [5, 6]. Among various synthetic methods spray pyrolysis method is employed to deposit the Mo doped NiO thin films due to easy to handling and control over the deposition parameters. In the present study, we report on the synthesis and characterization of pure and Mo doped NiO thin films by spray pyrolysis technique. The structural and electrochemical properties of these NiO thin films have been reported and results obtained are discussed.

METHODOLOGY

Undoped and Molybdenum doped Nickel oxide (Mo-NiO) thin films were prepared by spraying 0.1 M aqueous solution of nickel nitrate Ni $(NO_3)_2$ mixed with molybdenum trioxide powder (MoO_3). The doping percentage of Mo in the deposited films was varied: 2, 4, 6, 8 and 10 wt. % (denoted as NR_1, NR_2, NR_3, NR_4 and NR_5) onto ultrasonically cleaned glass substrates and FTO coated substartes at temperature 370 °C. The temperature was optimized in our previously published article [7]. All the deposition parameters like spray rate (5 ml/min), nozzle to substrate distance (NSD) (32 cm), carrier gas flow rate, etc., were kept at their optimized values. X-ray diffraction (XRD) patterns obtained with CuK_α (λ = 1.54 Å) radiation from a Philips X-ray diffractometer model PW1710 in the span of angle 20-80°. The electrochemical experiment is carried out in the three electrode cell consisting of platinum as counter electrode and Ag/AgCl as reference using potentiostat (CHI 6005E) instruments.

RESULTS AND DISCUSIONS

X-ray Diffraction analysis

The XRD patterns of the synthesized undoped and Mo doped NiO samples are shown in Fig. 1. All reflections are polycrystalline in nature assigned to the cubic structure in pure NiO with (1 1 1) as preferential orientation and rhombohedral structure in doped NiO with preferred grain orientation along the (2 0 2) plane and weak reflection along (0 2 1). No characteristics peak corresponding to either molybdenum, nickel or any of its oxides were observed in the XRD graph, which indicates that there is no any other phase present in Mo-doped NiO thin films. This suggests that the incorporation of Mo ions into the NiO lattice. Low full width at half maximum (FWHM) at 2% Mo doping concentration suggests that good crystalline quality of NiO thin films.

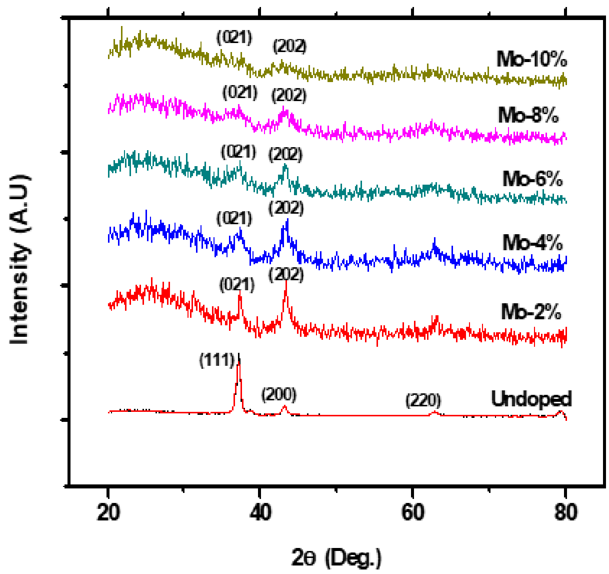


Figure 1 (a) X-ray diffraction pattern of Mo doped NiO thin film electrodes at different doping concentrations. (b) Variation of FWHM and crystallite size with respect to the doping concentration of Mo.

On doping of Mo, intensity of the (2 0 2) plane decreases and FWHM increases which indicates films losing crystallite quality. The parameters such as grain size (D), dislocation density (δ) and microstrain (ε) were calculated using following formulae's [8]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

$$\delta = \frac{1}{D^2} \quad (2)$$

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

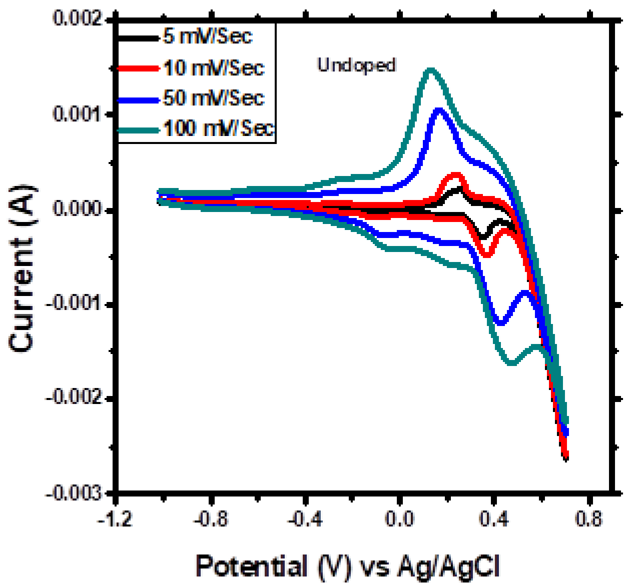
Where, k is the shape factor with value k=0.94, λ is wavelength of X-ray used (λ=1.5406 Å), β is the peak width, θ is the angle of diffraction. Table.1 shows the microstructural properties of Mo doped NiO thin film electrodes at different doping concentrations. One of the possible reason for decrease the crystalline quality at high doping concentration may be difference in ionic radii because when large number of Mo replaces Ni in lattice, distortion is sharpen resulting in larger strain is developed in the films and consequently affecting the normal growth of NiO crystals.

Cyclic Voltammetry

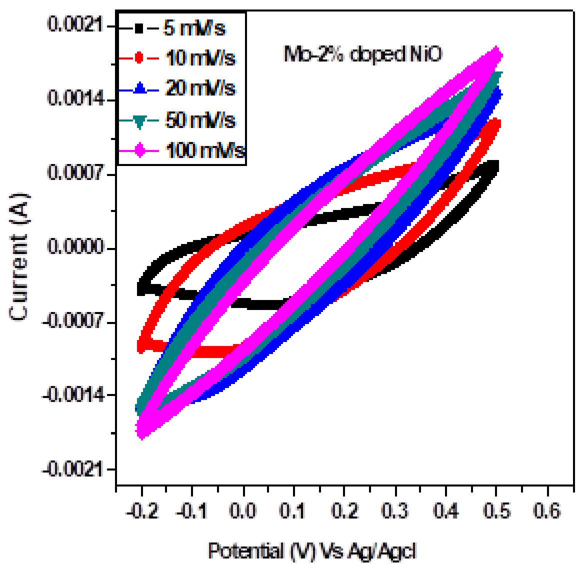
Figure 2(a, b) shows the cyclic voltammograms (CVs) of undoped and 2% Mo doped NiO thin film deposited at substrate temperature 370 °C in a potential range of -1 V to +0.7 in pure NiO and -0.2 to +0.5V vs. Ag/AgCl at scan rates 5mV/s in doped NiO. It is found that, as the scan rate increases the area under curve increases but the specific capacitance decreases. All curves of the 2% Mo doped NiO electrode at all scan rates without any redox peaks exhibits elliptical shape, indicating the presence of a typical EDLC-type behavior wheares in pure NiO well resolved oxidation reduction peak were observed which shows the nature pseudocapacitor. The absence of any peaks in CV curves indicates a faster charging/discharging in the Mo doped NiO electrode.

Table 1. Microstructural Properties of Mo doped NiO thin film electrodes of (1 1 1) and (2 0 2) plane in pure and doped NiO at different doping concentrations.

Doping Concentration (%)	FWHM	Grain Size (nm)	Dislocation Density (Lines/m²)	Micro Strain
0	0.0152	11.2434	7.91×10^{15}	3.6083
2	0.0018	17.75	31.71×10^{14}	0.19514
4	0.96	15.52	41.47×10^{14}	0.22314
6	0.5846	25.49	15.38×10^{14}	0.13589
8	0.3762	39.63	6.36×10^{14}	0.08742
10	0.1575	94.69	1.11×10^{14}	0.03659



(a)



(b)

FIGURE 2 (a) Cyclic Voltammetry curves of undoped NiO thin film electrodes at different scan rates. (b) Cyclic Voltammetry curves of 2% Mo doped NiO thin films

The specific capacitance value is calculated by the expressions:

$$C = \frac{I}{dV/dt}, \quad C_i = \frac{C}{A}, \quad C_s = \frac{C_i}{m} \qquad \textbf{(4)}$$

where, I (A) average charge deduced from CV, dV/dt (mV/s) is the voltage scan rate, A (cm^2) and m (g) are area of the electrode surface and mass of the active material deposited on the electrodes, respectively. The obtained specific capacitance values are 620 Fg^{-1} and 1000 Fg^{-1} in doped and pure NiO at 5 mV/s respectively. As the scan rate increases specific capacitance decreases which is due to ion exchange mechanism [9]. Fig. 2(b) shows the variation of specific capacitance with scan rates. As the scan rate increases capacitance values decreases.

CONCLUSION

Undoped and Mo doped NiO thin films were synthesized by chemical spray pyrolysis method at different doping concentrations and effect doping concentration on structural and electrochemical properties were investigated. X-ray diffraction results reavels that all the deposited films are polycrystalline in nature with cubic crystal structure in pure NiO and rhombohedral structure in doped NiO. XRD graphs reveal that the films loose crystallinity with increase in doping concentration. The value of specific capacitance in pure NiO (1000 Fg^{-1}) is more than that of doped NiO (620 Fg^{-1}).

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