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Preparation and characterization of spray deposited $NiMoO_4$ thin films for photovoltaic electrochemical studies

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Abstract

The preparation of nickel molybdate ($NiMoO_4$) thin film by spray pyrolysis with ammonical solution as a precursor is presented. The phase and surface morphology characterizations have been carried out by XRD and SEM analysis. The study of optical absorption spectrum in the wavelength range 350–850 nm shows direct as well as indirect optical transitions in the thin film material. The dc electrical conductivity measurements in the temperature range 310–500 K indicate semiconducting behavior of the thin film with high resistivity (10^7 Ω cm) at room temperature. The thin films deposited on fluorine doped tin oxide (FTO) coated conducting glass substrates were used as a photoanode in photovoltaic electrochemical (PVEC) cell with configuration: $NiMoO_4$ $|Ce^{4+}, Ce^{3+}|$ Pt; 0.1 M in 0.1N H_2SO_4. The PVEC characterization reveals the fill factor and power conversion efficiency to be 0.48 and 0.81%, respectively. The flat band potential is found to be −0.39 V (SCE).

Keyword: A. Oxides; A. Thin films; C. Electron microscopy; C. X-ray diffraction; D. Electrochemical properties

1. Introduction

Nickel molybdate ($NiMoO_4$) is an interesting compound because of its structural, electronic and catalytic properties [1–4]. It is a well-known active catalyst for oxidation reaction [5] and particularly for the oxidative dehydrogenation of propane to propene [6]. The catalytic property of $NiMoO_4$ is closely related to its structure [7]. $NiMoO_4$ belongs to a series of isostructural compounds $AMoO_4$ with A representing a divalent cation: A = Fe, Mn, Co and Zn. Two phases of $NiMoO_4$ can be observed at atmospheric pressure [8]. Both phases are monoclinic with space group *P*2/*m*. The phase, stable at room temperature, has the structure of α-$CoMoO_4$ [9] with Mo in a distorted octahedral site [10]. The phase β, stable at higher temperature has the structure of α-$MnMoO_4$ [11] with Mo in a distorted tetrahedral site. The β-phase of $NiMoO_4$ is almost twice more selective for dehydrogenation of propane to propene than the α-phase [7]. Steinbrunn et al. [12] carried out the electrical conductivity measurements on the $NiMoO_4$ ceramic samples and confirmed the existence of two polymorphic forms of $NiMoO_4$. Furthermore, Thomas et al. [13] have studied the dependence of catalytic activity of $NiMoO_4$ on its defect properties studied by electrical conductivity measurements. A literature survey revealed that $NiMoO_4$ has been used as a photoanode material in the form of polycrystalline pellet in photoelectrochemical (PEC) cell [14].

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PEC cells are devices in which solar energy is converted into either electrical or chemical energy by electrochemical effects. It has been observed that the PEC properties of the samples depend, to a large extent, on the methods of preparation [15]. Moreover, the photocurrent of the PEC cell depends upon the internal bulk resistance of the semiconductor and the width of the space charge layer. If the semiconductor electrode of PEC cell is a polycrystalline pellet, the bulk resistance, will depend upon the density and the thickness of the pellet, and on the concentration of the donor levels (N_D) in the pellet. Also, the space charge layer thickness will depend inversely on the donor concentration, N_D. Therefore, in a pellet it becomes difficult to meet these two opposing requirements, i.e. to maintain a low bulk resistance and a high space charge layer thickness, simultaneously. In addition, the reproducibility of the results from one pellet to the other is also problematic. However, in the case of a thin film electrode one can hope to get large space charge width at low donor concentration without increasing the bulk resistance too much. Considering all these factors it is always preferable to use a thin film of thickness such that all the incident radiation is fully absorbed within the space charge region [16]. To the author's knowledge, no report has been found so far on the thin film deposition of $NiMoO_4$ and its characterization.

Therefore, it was thought worthwhile to deposit thin films of $NiMoO_4$ by spray pyrolysis (SP) process because of its simplicity, inexpensiveness, suitability for mass production [17] and extensive use in deposition of oxide materials [18–20]. In this communication we have investigated the structural, optical and electrical properties of $NiMoO_4$ thin films deposited on glass substrate by SP process and finally used the $NiMoO_4$ thin films deposited on conducting glass substrate as photoanode in photovoltaic electrochemical (PVEC) cell. PVEC cell consists of a semiconductor as photoelectrode, an inert metal electrode and an electrolyte. The electrolyte contains a redox couple, thus, after illumination oxidation takes place at the semiconductor photoanode and exactly opposite reaction occurs at the cathode, so that the composition of the electrolyte remains unchanged. Consequently, there is zero variation in the free energy of the total process.

2. Experimental

2.1. Thin film preparation

$NiMoO_4$ thin films were deposited on glass substrate obtained from Blue-Star, India by SP process using an apparatus described elsewhere [21]. The precursor solution for $NiMoO_4$ thin film is the ammonical solution of the green colored powdered material synthesized by precipitation method [6]. The substrate used for thin film deposition was ultrasonically cleaned, acetone-treated glass slide. A 25 mL of the precursor solution of 0.05–0.125 M was sprayed through a specially designed glass nozzle onto the heated glass substrates held at various temperatures ranging from 300 to 450 °C. Compressed air was used as carrier gas. The flow rate, deposition time, nozzle to substrate distance and frequency of the to–fro motion of the nozzle were kept constant at 5 mL/min, 5 min, 40 cm and 0.29 Hz, respectively. After the deposition, the thin films at ambient temperature were allowed to cool slowly to room temperature and then taken out for further characterizations.

2.2. Material characterizations

The as deposited films were first examined under an optical microscope (Leitz Orthoplan Microscope, Switzerland) to confirm the film deposition pattern, its uniformity and adherence to the substrate. The thin films obtained were then sintered in air atmosphere at temperatures 350–450 °C for crystallization, since the as deposited films prepared onto preheated substrates are always amorphous [22]. These sintered thin films were then subjected to X-ray diffraction (XRD) studies (Philips PW-1710 X-Ray diffractometer) using Cu Kα (radiation source) anode for structural characterization and phase identification. Surface morphology of the films was studied with scanning electron microscope (SEM), model JXA-840A, from JEOL, Japan with acceleration voltage 20 kV. A gold coating was deposited on the samples to avoid charging of the surface. The film thickness was determined by the weight difference consideration method [23]. Optical absorption and transmission studies were carried out using Hitachi spectrophotometer (UV–vis, NIR model 330, Japan) in the wavelength range 350–850 nm. To study the electrical properties of the thin films, dark resistivity measurements were taken using the two point probe method in the temperature range 310–500 K. Silver paste was applied to provide ohmic contact with the film [24].