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Electrosynthesis of molybdenum oxide thin films onto stainless substrates

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Abstract

The electrodeposition of uniform, nanocrystalline and highly oriented molybdenum oxide thin films was investigated at room temperature onto stainless steel substrates using citric acid as a complexing agent. The electrodeposition process of molybdenum oxide thin films from molybdic acid of various concentrations onto stainless steel substrate were studied by utilizing the electrochemical techniques. The prepared films were characterized for their structural, surface morphological and compositional properties by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray analysis. X-ray diffraction and transmission electron microscopy experiment reveals that the films are of crystallized size. XRD experiment showed that the crystallized product is composed of molybdenum oxide with dominant orientations of MoO_3.

Keywords: Thin films; Electrodeposition; Growth process; Molybdenum oxide

1. Introduction

Molybdenum oxide is a wide band gap n-type semiconductor that acts as catalyst in many reactions involving hydrogen and oxygen molecules [1–6]. It plays an important role in technical applications because of its interesting structural and electronic surface properties. Many investigations have been carried out on the use of MoO_3 film in practical electronic display (ECD) devices. MoO_3 thin films have been found to be very sensitive to various gases such as NO, NO_2, CO, H_2 and NH_3 in temperature range of 300–600 °C [7–9]. Molybdenum trioxide exhibits new optical absorption bands (i.e. shows a new color) after it is irradiated with UV light. This effect has resulted in numerous applications in large area displays, high-density memory devices, smart windows, and so forth [10–17]. One of the most interesting applications of MoO_3 is known as smart windows in which the device must regulate the amount of light going through it. Nanocrystalline MoO_3 has been investigated for its outstanding performance in load-independent friction application [18]. Orthorhombic molybdenum trioxide (O-MoO_3) exhibits a unique layered structure in which each Mo atom is surrounded by distorted octahedron of oxygen atoms. Two layers of MoO_6 octahedral sharing all equatorial corners are joined together and stacked one over other. Hexagonal molybdenum trioxide (h-MoO_3) is a meta-stable phase of molybdenum oxides. The structure whose basic building unit is still a distorted octahedron of MoO_6, however, belonging to one of ReO_3 type, consists of a three dimensional array of corner shearing MoO_6 octahedrons. Crystalline molybdenum oxide (MoO_3) has shown interesting lithium intercalation properties [19,20]. Both of its open structure and the case of creating oxygen vacancies in the structure make it an ideal candidate for lithium secondary batteries [21,22].

Several methods have been used to prepare such as thermal evaporation, sputtering, chemical vapor deposition (CVD), flash evaporation [23–29]. Aside from these high-energy consuming, capital-intensive deposition techniques, less costly, lower temperature electrodeposition

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methodologies are also attractive since they offer several advantages. Cathodic electrodeposition of thin films of various metal oxides such as ZrO_2, CeO_2, TiO_2, Cu_2O and ZnO from aqueous solution was successfully achieved [30]. In some cases, the deposition leads to direct formation of crystalline thin films under near room temperatures. Other technological advantages generally found for the electrodeposition are simplicity and economy, rigid control of film thickness, uniformity and deposition rate and possibility of deposition onto substrates of complex shape. Electrodeposition of molybdenum oxide has been investigated by several groups [31–36]. Guerfi et al. [31] studied electrochemical, spectroscopic, structural and stability of electrodeposited MoO_3 thin films. The films were prepared from metal/hydrogen pyroxide solution on transparent conducing glass. The as-deposited films are of hydrated molybdenum oxide and the films showed a improvement in crystallinity after a heat treatment in air (260 °C). McEvoy and Stevenson [32,33] and McEvoy et al. [34] reported cathodic electrodeposition of molybdenum oxide from aqueous solution of iso-polymolybdates and peroxo-polymolybdates and studied reaction mechanism using different characterization tools. Dong and Wang [35] and Liu et al. [36] reported mixed-valent molybdenum (VI, V) oxide film grown on carbon substrates by the electrodeposition. The films were deposited by cycling the potential between +0.2 and −0.7 V vs SCE in Na_2MoO_4 solution.

The purpose of the work reported here was to study electrodeposition of molybdenum oxide thin films on stainless steel substrates from aqueous solutions. The molybdenum oxide films were further characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X-ray analysis techniques for their structural, morphological and compositional studies.

2. Experimental

2.1. Molybdenum oxide thin film preparation

Molybdenum oxide thin films were electrodeposited from an aqueous solution of molybdic acid with and without complexing agent (citric acid). All solutions were prepared by dissolving the requisite amount of molybdic acid in water which is distilled twice and then treated with a millipore Milli Q system. The solutions were de-aerated by argon bubbling before each experiment. The molybdic acid solutions of different concentrations viz. 50, 10, 5, 1, 0.5, and 0.1 mM was prepared. 1 M citric acid solution was prepared by dissolving the requisite amount of citric acid in triple distilled water. Stainless steel (SS) substrates were used for the deposition of molybdenum oxide thin films. The SS substrates were mirror polished with smooth polishing paper, cleaned with detergent and finally cleaned ultrasonically in triple distilled water. A standard three-electrode glass cell was utilized for electrochemical measurements. A high purity graphite plate of area 4 cm^2 was used as a counter electrode. Ag/AgCl was used as reference electrode, to which all the measured potentials were referred. SS substrates of area 1×1 cm^2 were used as working electrodes. The spacing between working electrode and counter electrode was 1 cm. All the experiments were performed at room temperature. Molybdenum oxide deposition onto SS substrates was studied by means of cyclic voltammetry (CV) technique. The CV for all the concentrations was initially carried between −1.4 and +0.8 V at the scan rate of 20 mV s^{-1}. After deposition, the films were rinsed in triple distilled water, and preserved in a desiccator. Thickness of the film was measured by using cross-sectional SEM analysis. The thickness of the film is about 500 nm for 1200 s deposition time. The color of the film was blackish. The as-deposited films without complexing agent have cracks. In many cases, citrate is used in order to establish electrodeposition conditions that lead to homogeneous deposits with different compositions. Citrate in the electrolyte assures that the pH remains stable during the deposition process [37].

2.2. Characterization of molybdenum oxide thin film

Potentiostatic measurements were performed using an EG and G (VersaStat-II) controlled by a personal computer. The software used to perform the electrochemical experiments was M270 from EG and G PARC. X-ray diffraction pattern of molybdenum oxide films were obtained by using X-ray diffractometer (RINT/PMAX 2500, Rigaku, Japan) in the range of scanning angle 10–90 (2θ) deg with Cu Kα radiations. Surface morphological studies were carried out with scanning electron micrographs, obtained with FE-SEM, (SM-6340 F, Jeol, Japan). TEM images were obtained with Philips CM-30 TEM unit (point resolution = 2.4 Å) with acceleration voltage of 300 kV coupled with EDAX-DX-4 analyzer. The semi-quantitative elemental composition of the film was determined using energy dispersive X-ray (EDAX) analysis using horida-ex-200, Japan, with spatial resolution of 134 eV.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows typical cyclic voltammetric curves obtained for SS (substrates) electrodes in molybdic acid electrolyte solutions of various concentrations. A typical CV recorded for 50 mM solution concentration is shown in Fig. 1a. The voltammogram clearly depicts the well-defined cathodic (E_c) peaks at −608 mV. The voltammogram shows a cross-over between cathodic current branches, which is a characteristic of the nucleation process. Fig. 1b–e shows CVs recorded at different solution concentrations ranging from 10 to 0.1 mM. The CV peak current usually increases linearly with increase in solution concentration. However, in present case, the nonlinear increase in peak current with increase in solution concentration was observed. This lack