Structurally and mechanically tunable molybdenum oxide films and patterned submicrometer structures by electrodeposition

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ABSTRACT

1.5 μm-thick molybdenum oxide films have been electrodeposited potentiostatically from 0.2 M Na_2MoO_4 electrolyte onto indium tin oxide (ITO)/glass substrates at pH = 1, 6 and 9. The influence of cetyltrimethylammonium bromide (CTAB) surfactant on films' adhesion, morphology, degree of porosity, molybdenum speciation, and crystallographic structure has been systematically investigated. The addition of CTAB (0.01 M) to the bath clearly improves film adherence to the substrate, reduces cracking, and increases crystallinity. This has an impact on the physical properties of the films. In particular, both hardness (H) and Young's modulus (E) increase, as determined from nanoindentation tests. The growth of ordered arrays of molybdenum oxide submicrometer structures, including pillars and stripes, by electrodeposition onto e-beam lithographed Au/Ti/Si substrates is also reported.

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1. Introduction

Transition metal oxides in thin-film form have received much attention owing to their promising applications in electrochromics, energy storage, sensing, and non-volatile resistive random access memory devices, among others [1–3]. Molybdenum oxide is a suitable candidate in many of these applications due to its unusual chemistry produced by multiple Mo valence states (IV, V and VI) and a rich variety of crystallographic structures [3,4]. MoO_2, with its distorted rutile structure, presents a high metal-like conductivity [5] and it finds uses as anode material in solid oxide fuel cells [6]. In addition, its layered structure makes it suitable as ion intercalation/deintercalation host in, for instance, lithium batteries [3,7]. MoO_3 is an n-type semiconductor with two most common crystal phases: the thermodynamically stable orthorhombic α-MoO_3 and the metastable monoclinic β-MoO_3, that show optical switching upon thermal, photo (photochromism) [8–10] or electric (electrochromism) [11,12] excitations. Such an optical modulation (colouration/bleaching) is effectively used in many applications like smart windows and antidazzling coatings [13]. The crystallinity degree is an important asset depending on the end application. For example, amorphous molybdenum oxide is suitable as an electrochemical sensor for iodate ions [14], whereas MoO_3 nanocrystalline films and nanorods can serve as gas sensors toward H_2 [15] and NO_2 [16], respectively. In addition, nanostructured α-MoO_3 has been applied as supercapacitor electrodes in acid aqueous electrolytes [17]. For all these reasons, controlling both the valence state and the crystallographic structure of the molybdenum oxide materials is of prime importance to meet the required technological demands.

So far, molybdenum oxides have been prepared by a variety of physical and chemical techniques: pulsed laser deposition [18], chemical vapour deposition [19], sputtering [20], thermal evaporation [21], spray pyrolysis [22], electrodeposition [23,24], anodization [25], and sol-gel [26]. Electrochemical methods are advantageous for several reasons. They are generally easy to perform and can be readily used to tailor films' properties. In particular, electrodeposition offers facile control over thickness, morphology, extent of oxidation and doping of the films at ambient pressure. The influence of bath formulation and growth conditions on the oxidation state of molybdenum oxide films has been studied in detail in the past [3]. McEvoy and Stevenson described the cathodic electrodeposition of MoO_3 from acidic peroxo-polymolybdate solutions onto indium-doped tin oxide (ITO) electrode [27]. The same authors deeply investigated the mechanism of molybdenum oxides deposition using different tools, namely chronocoulometry and quartz crystal microbalance techniques

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[28,29]. The authors showed that a graded reduction of molybdenum precursors toward amorphous hydrates of non-stoichiometric, mixed-valent molybdenum oxides takes place from acidic peroxo-polymolybdate solutions. Patil et al. explored the electrosynthesis of hydrous amorphous MoO_2 thin films from an alkaline solution containing ammonium molybdate (pH = 9) [11]. Layered films consisting of mostly Mo(IV) were obtained from citrate-molybdate solutions at pH = 8.3 by applying different potentials [23]. The potentiostatic deposition of molybdenum oxides with mixed valence states of Mo(V) and Mo(IV) was also described in citrate-molybdate electrolytes at pH = 6.6 [30]. From literature screening, it is evident that bath pH is a key parameter in determining the Mo oxidation state in the films. Nevertheless, other parameters also have an effect on the oxidation state of electrodeposited molybdenum oxide, such as the deposition technique. For example, it was found that MoO_3 films deposited at pH = 1 by cyclic voltammetry contained a mixture of Mo^V and Mo^{VI} and were less homogeneous than those obtained potentiostatically, for which only Mo^{VI} was detected [31]. Also, the crystallinity and phases obtained are very sensitive to the electrodeposition conditions. It was found that the sweep rate in cyclic voltammetry experiments determined the formation of either α- or β-MoO_3 [24]. Remarkably, X-ray diffraction analyses indicate that the films are typically amorphous (or poorly crystalline) in the as-deposited state [11,24,27]. Therefore, annealing at temperatures equal to (or beyond) 250 °C is typically required to achieve fully crystalline films [11,27]. Guerfi et al. [32] showed that an increase in crystallinity of the as-deposited molybdenum oxide is possible after heat-treating the films in air at 260 °C and that complete crystallization occurs at 300 °C.

In order to favour the growth of fully crystalline molybdenum oxide deposits without the need for a heat-treatment, additives can be added to the bath. Additives usually play an important role in electrodeposition processes as they bring or change some microstructural features of electrodeposited materials. Cetyltrimethylammonium bromide (CTAB) is a cationic surfactant widely used in electrodeposition. In particular, it is known to be a corrosion inhibitor [33] and grain refiner [34] in metals electrodeposition. Also, it is used as templating agent for the electrochemical production of metal oxide foams [35,36]. Thus, it is envisaged that the addition of CTAB to the electrolyte could impact molybdenum oxide film growth and, in turn, modulate molybdenum oxidation state, crystallographic structure, film adhesion, and porosity.

In spite of numerous studies paying attention to the physicochemical properties and applications of molybdenum oxides, only few works have investigated their mechanical properties [37] and, to the best of our knowledge, none of them are related to the mechanical behaviour of electrodeposited molybdenum oxide films. Actually, since the adherence of electrodeposited molybdenum oxide films to the substrate is poor or either the layers feature cracks, the measurement of their mechanical properties by micro- or nanoindentation is certainly not straightforward. This has probably precluded any detailed study in the field.

With the continuing trend toward miniaturization of devices, electrodeposition has been typically combined with polycarbonate/aluminum oxide membranes and e-beam lithographed substrates to obtain patterned arrays of nanostructures. Ordered arrays of Mo oxide nanowires have been recently produced by Inguanta and co-workers on commercial track-etched polycarbonate membranes [38]. Examples of patterned nanostructures obtained by electrodeposition on e-beam lithographed substrates can be found in the literature, especially for magnetic metals and alloys [39]. However, there is a dearth of literature on template-assisted electrodeposition of metal oxides on pre-patterned substrates.

In this work, molybdenum oxide films have been potentiostatically deposited onto ITO/glass substrates and the effect of CTAB additive onto films' morphology and structure at three different pH values has been explored. Our results reveal that CTAB improves the adherence of the deposits to the substrate and thus consistently facilitates the measurement of relevant mechanical parameters, like hardness or Young's modulus, by means of nanoindentation. Furthermore, the preparation of ordered arrays of molybdenum oxide submicrometer structures –pillars and stripes– by template-assisted electrodeposition is presented.

2. Experimental techniques

Molybdenum oxide films were obtained potentiostatically by direct current electrodeposition in one-compartment thermostatized three-electrode cell using a PGSTAT120N Autolab potentiostat/galvanostat (Ecochemie). ITO-coated glass (surface resistivity 30-60 Ω/sq.) was used as working electrode (WE) in both cyclic voltammetry (CV) experiments and potentiostatic deposition. In all cases the WE was positioned vertically within the electrolyte. The working area was set between 0.2 and 0.4 cm^2. A Ag|AgCl (3 M KCl) (E=+0.210 V versus standard hydrogen electrode (SHE)) reference electrode (Metrohm AG) was used. A platinum sheet served as the counter electrode. Molybdenum oxide films were deposited from an electrolyte containing either 0.2 M $Na_2MoO_4 \cdot 2H_2O$ (labeled as "no add" bath) or 0.2 M $Na_2MoO_4 \cdot 2H_2O$ + 0.01 M $C_{19}H_{42}BrN$ (labeled as "CTAB" bath). The electrolyte volume was 50 mL. Analytical grade reagents and ultrapure water (18 MΩ cm) were used to prepare the plating solution. The pH values selected were 1, 6 and 9. The pH was adjusted with either H_2SO_4 or NaOH. Potentiostatic deposition was applied under mild stirring (100 rpm) using a magnetic stirrer bar. The temperature of the bath was set at 25 °C. The electrical charge was adjusted across all depositions to attain similar film thicknesses (approximately 1.5 μm). Prior to deposition, the ITO surface was first degreased with acetone and later rinsed with ultrapure water. Before and during each deposition, the electrolyte was deaerated with argon gas flow.

For the growth of ordered arrays of molybdenum oxide submicrometer structures, e-beam patterned Au/Ti/Si substrates were used as the cathode. First, Ti (100 nm)/Au (400 nm)/Ti (15 nm) were evaporated onto Si(111) substrates. An electron sensitive resist (ZEP-520A) of about 500 nm in thickness was then spin-coated onto the substrate and patterning was carried out by electron-beam lithography (EBL) with the CRESTEC CABL-9500C electron-beam lithography machine. Arrays of cylindrical holes of 200 nm and 500 nm in diameter and stripes of 100 nm, 500 nm and 1 μm width (15 μm lengths) were patterned. Following the lithographic procedure, the resist was developed in anisol. Before electrodeposition, all samples were submerged in HF solution for 1 min to remove the upper 15 nm-thick Ti layer to allow the deposition of molybdenum oxide directly onto the Au surface. Finally, the substrates were dipped in diluted sulphuric acid to remove oxides and organic residues. The Au/Ti/Si substrates were then immersed in the electrolyte for 10 min before deposition was started. After electrodeposition, the resist was etched with dimethylacetamide at 35 °C for 1 min.

The morphology of the deposits was examined by field emission scanning electron microscopy (FE-SEM) using a Zeiss MERLIN microscope operated at 1.2 kV to prevent from charging effects. Energy dispersive X-ray (EDX) analyses were carried out at 15 kV. The crystallographic structure of the films was studied by X-ray diffraction (XRD). XRD patterns were recorded on a Philips X'Pert diffractometer using the Cu Kα radiation, in the 10°–70° 2θ range (0.03° step size, 10 s holding time). Complementary transmission electron microscopy (TEM) observations were carried out on a Jeol-