

Growth and surface characterization of sputter-deposited molybdenum oxide thin films

C.V. Ramana^{a,*}, V.V. Atuchin^b, V.G. Kesler^c, V.A. Kochubey^b, L.D. Pokrovsky^b,
V. Shutthanandan^d, U. Becker^a, R.C. Ewing^a

^aNanoscience and Surface Chemistry Laboratory, Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA

^bLaboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia

^cTechnical Centre, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia

^dEnvironmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA

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Abstract

Molybdenum oxide thin films were produced by magnetron sputtering using a molybdenum (Mo) target. The sputtering was performed in a reactive atmosphere of an argon–oxygen gas mixture under varying conditions of substrate temperature (T_s) and oxygen partial pressure (pO_2). The effect of T_s and pO_2 on the growth and microstructure of molybdenum oxide films was examined in detail using reflection high-energy electron diffraction (RHEED), Rutherford backscattering spectrometry (RBS), energy-dispersive X-ray spectrometry (EDS), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) measurements. The analyses indicate that the effect of T_s and pO_2 on the microstructure and phase of the grown molybdenum oxide thin films is remarkable. RHEED and RBS results indicate that the films grown at 445 °C under 62.3% O_2 pressure were stoichiometric and polycrystalline MoO_3 . Films grown at lower pO_2 were non-stoichiometric MoO_x films with the presence of secondary phase. The microstructure of the grown Mo oxide films is discussed and conditions were optimized to produce phase pure, stoichiometric, and highly textured polycrystalline MoO_3 films.

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1. Introduction

Transition metal oxides with diverse structures, properties, and phenomena have been the focus of much attention in recent years in view of their scientific and technological applications. Molybdenum oxide (MoO_3), among the other transition metal oxides, exhibits interesting structural, chemical, electrical, and optical properties [1–12]. MoO_3 finds application as a cathode material in the development of high-energy density solid-state microbatteries [4,5]. MoO_3 is considered as a chromogenic material as it exhibits electro-, photo-, and gaso-chromic (coloration) effects by virtue of which the material is of much interest for the development of electrochromic display devices, optical switching coatings, display devices, and smart window technology [1–3,6–10]. Molybdenum oxide films and nano-

crystals also find application in sensors and lubricants [11–13]. In all these technological applications, optimization of the growth conditions to produce phase pure MoO_3 thin films with controlled structure, surface texture and morphology, and optical and electronic properties are highly important. Therefore, improved understanding of the growth, microstructure, and surface features as a function of growth conditions and factors affecting these physical properties is a prerequisite.

MoO_3 exists in two crystalline polymorphs, the thermodynamically stable orthorhombic α - MoO_3 and the metastable monoclinic β - MoO_3 phase. The two polymorphic phases of MoO_3 (α , β) are represented in Fig. 1. The α - MoO_3 (Fig. 1a) crystallizes with orthorhombic symmetry ($a = 1.3855$ nm, $b = 0.3696$ nm, and $c = 0.3963$ nm) with four formula units per unit cell [14,15]. The α - MoO_3 single-phase can be represented as a double layers of linked distorted MoO_6 octahedra parallel to (0 1 0) planes. Within each double layer MoO_6 octahedra form edge-sharing zig-zag rows along the [0 0 1] direction and corner-sharing rows along [1 0 0]

* Corresponding author.

E-mail address: ramanacv@umich.edu (C.V. Ramana).

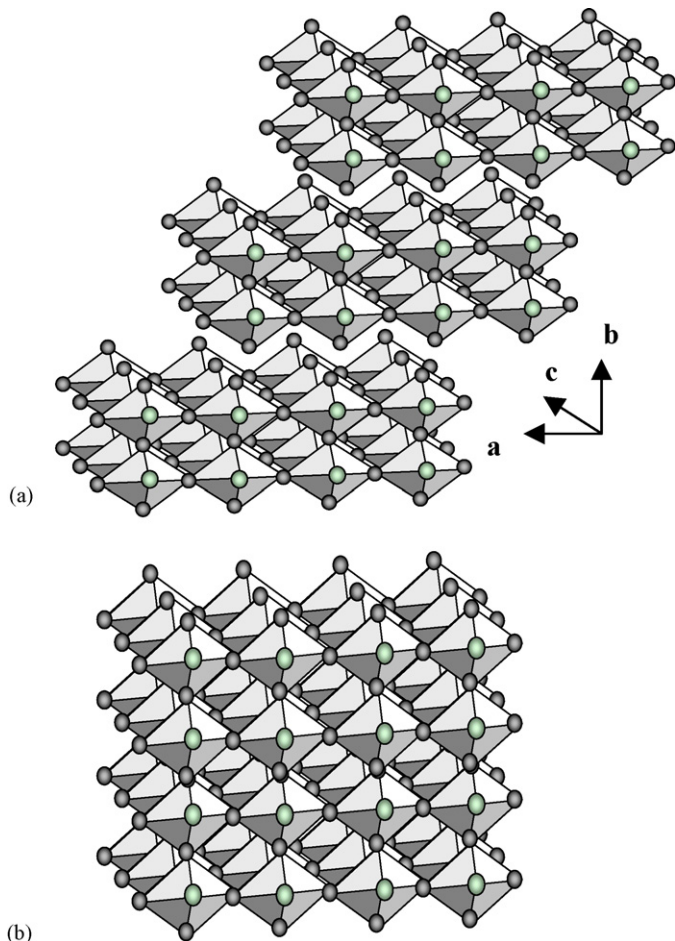


Fig. 1. Schematic representation of the structure of MoO_3 phases: (a) the layered α - MoO_3 phase with an orthorhombic lattice differs from the β - MoO_3 phase; (b) with a monoclinic lattice related to the three-dimensional ReO_3 structure.

direction. Successive layers are held together by weak interlayer forces with easy cleavage along (0 1 0) planes. The β - MoO_3 phase (Fig. 1b) with a monoclinic symmetry ($a = 0.7122$ nm, $b = 0.5366$ nm, $c = 0.5566$ nm, and $\beta = 92.01^\circ$) does not contain the van der Waals gap of α - MoO_3 [16].

It is highly desirable to have complete understanding of the composition, structure, and phase of the grown Mo oxide films since the properties and performance of the resulting films are mainly governed by their microstructure. The synthesis of crystalline MoO_3 films requires higher temperatures, where the compositional deviation is very common resulting in the formation of layers with Mo in the reduced state [4–14,17]. In the present work, an attempt has been made to grow thin layers of Mo oxides using a sputtering technique. The purpose of this work is to establish and optimize the growth conditions to produce Mo oxide films for optical and electrochemical applications. The grown films were characterized by a wide variety of surface/interface analytical techniques in order to obtain the complete information on the surface and film crystal structure, topography, composition, phase, and morphology. Using the results obtained and presented in this paper, we show that the stable and single-phase α - MoO_3 films, without any

compositional deviation, can be grown using sputtering even at higher temperatures ($>400^\circ\text{C}$).

2. Experimental

2.1. Film deposition

The Mo oxide films were prepared by dc reactive sputtering using a 100 mm Mo metal (99.95%) target. The sputtering was performed in an atmosphere of argon (Ar) and oxygen (O_2) mixture. The deposition chamber was evacuated to achieve an initial base pressure of 5×10^{-6} Torr prior to film fabrication. The target electrode was set in the left side of the vacuum chamber and was water cooled. The constant power used was 170 W at sputtering current of 320 mA. The deposition was made on to well-cleaned Si (1 0 0) substrates. Both p- and n-type Si substrates were employed in order to test the variation in growth behavior. The substrates were attached to a thick copper holder which can be heated by three halogen lamps up to 650°C . The temperature was controlled using a thermocouple attached to the substrate holder and stabilized at the desired temperature (T_s) to an accuracy of $\pm 2^\circ\text{C}$. In order to have precise control of the sputtering flow, the holder was installed at 230 mm from the cathode, at a sufficient distance from the gas discharge zone. In this geometry the reactive MoO_3 film formation is governed only by thermochemical oxidation of Mo atoms by oxygen on the surface of the heated substrate. Research-grade argon and oxygen were admitted into the reaction chamber through variable leak valves. The thickness of the films was measured with optical interferometry method.

The optimization of T_s for our work using the present experimental set-up was performed by detecting the crystallinity of the sample. For $T_s < 350^\circ\text{C}$, no MoO_3 crystalline films were found for any oxygen partial pressure ($p\text{O}_2$). For $T_s > 500^\circ\text{C}$, the precipitation is not possible because of thermal activation of MoO_3 sublimation from the surface. Therefore, the T_s was stabilized at $445 \pm 2^\circ\text{C}$ to produce crystalline films of Mo oxide as a function of varying $p\text{O}_2$. The Ar- O_2 gas mixture for oxidation was varied in the range of 61.0–62.3% O_2 . The total operating pressure during deposition was 10^{-3} Torr. The time of deposition was 30 min resulting in a film thickness of 130 nm. The deposition rate was ~ 4.3 nm per minute. The source was turned off, after the sputtering process, and the sample was kept in the chamber for 6 min at $445 \pm 2^\circ\text{C}$ followed by cooling to room temperature for a duration of 12 h in pure Ar atmosphere at a pressure of ~ 1 Torr.

2.2. Film characterization

The grown Mo oxide thin films were characterized using a wide variety of experimental techniques. The surface crystallography was investigated using reflection high-energy electron diffraction (RHEED) measurements at the EFZ4 device (Carl Zeiss). An electron beam of energy 65 keV was directed at the sample surface and the images of the diffracted electrons were recorded to analyze the crystal structure of the films. Rutherford backscattering spectrometry (RBS) experiments were carried

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