



Structure evolution in reactively sputtered molybdenum oxide thin films



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ARTICLE INFO

Article history:

Received 1 December 2015

Received in revised form

1 July 2016

Accepted 2 July 2016

Available online 4 July 2016

Keywords:

Molybdenum oxide

Thin film

MoO₂

MoO₃

Reactive sputtering

ABSTRACT

The current work investigates structure and property relations of molybdenum oxide thin films deposited by reactive dc magnetron sputtering from a molybdenum target with varying oxygen/argon gas flow ratio during deposition. With increasing oxygen partial pressure, the film growth rate decreased from 90 to 7 nm/min, whereas the oxygen content in the films increased up to 75 at.%. The dominating phases found by X-ray diffraction and Raman spectroscopy were MoO₂, different polymorphs of Mo₄O₁₁, and MoO₃. The optical appearance changed from metallic to yellowish transparent with increasing oxygen content in the thin film, while the electrical properties varied from electrically conductive to insulating. In general, structure and properties of the deposited molybdenum oxide thin films are tuneable by adjusting the oxygen/argon gas flow ratio during deposition, which enables the use of these films in a wide range of optical and electronic applications.

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1. Introduction

Oxide thin films are used in a wide variety of industrial applications ranging from hard coatings to thin films in optical and electronic applications. Examples include Al₂O₃ used as a wear-resistant coating due to its high hardness and chemical inertness [1], TiO₂ due to photocatalytic properties [2] and transparent conductive oxide (TCO) materials like tin doped indium oxide (ITO) [3] or aluminium doped zinc oxide (AZO) [4,5]. By changing the stoichiometry or by alloying or doping the base materials, it is possible to tune the material properties according to the needs of the intended applications.

Different deposition techniques are employed to synthesise such thin film materials, e.g. chemical vapour deposition, sol-gel, printing, and physical vapour deposition techniques, in particular magnetron sputter deposition (MSD) [6]. MSD is a versatile deposition technique that can be used in direct current (dc), pulsed dc or radio frequency mode for the synthesis of a wide variety of materials including metals, nitrides, carbides, borides, sulfides or oxides. In the latter cases, reactive processes are frequently used, that

means a reactive gas, for example oxygen, is added to the process gas during the deposition process [7]. The stoichiometry of the synthesised thin film can be tuned by varying the partial pressure of the reactive gas [8]. The chemical compound is typically formed by reactions between adsorbed reactive gas molecules on the substrate and impinging target atoms enabling the growth of the thin film. At the same time, compounds will also be formed on the target surface and, as a consequence, alter the sputter behaviour. If the target is in the so-called “poisoned” mode, then the sputter and deposition rates are typically lower [9].

The Mo-O system is known to contain two stable oxides, MoO₂ and MoO₃, as well as several Magnéli phases with intermediate Mo/O ratios [10]. All these oxides occur in different colours [11,12] and they cover a wide range of electrical and optical properties depending on their oxidation state. The properties of molybdenum oxides vary from a non-transparent appearance with metallic-like electrical conductivity (MoO₂) to transparent and electrically insulating behaviour (MoO₃). The electrical conductivity of the Magnéli phases ranges from a metallic to a semiconducting behaviour [13]. From the entire range of molybdenum oxides, MoO₃ thin films are almost exclusively used in today's industrial applications like gas sensing [14], photovoltaic [15], electrochromic [16] and photochromic thin films [16,17]. The field of possible application for lower oxidised molybdenum oxide thin films remained

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largely unexplored so far.

This study was done in order to investigate the structure evolution in reactively sputtered molybdenum oxide thin films as a function of the oxygen partial pressure. The composition and structure of the synthesised films was analysed by electron probe microanalysis (EPMA) using wavelength-dispersive X-ray spectroscopy (WDS), X-ray diffraction (XRD) and Raman spectroscopy measurements. Details about the growth of molybdenum oxide thin films were obtained by scanning electron microscopy (SEM) top-view and cross-section imaging. The electrical resistivity and the optical appearance are discussed on the basis of changes of the film structure.

2. Experimental methods

The molybdenum oxide thin films were grown on (100)-oriented silicon (20 mm × 6 mm × 0.35 mm) and soda lime glass (20 mm × 6 mm × 1 mm) substrates by unbalanced dc-MSD. Prior to the deposition, the substrates were cleaned in ultrasonic baths of acetone and ethanol and dried with hot air. After mounting the samples on the rotatable substrate holder, the deposition chamber was evacuated to a base pressure below $1 \cdot 10^{-3}$ Pa and was baked out at 500 °C for 30 min. Subsequently, the temperature was decreased to 120 °C and the targets were sputter-cleaned in pure Ar atmosphere for 5 min, while a shutter shielded the substrates to prevent deposition of Mo on them in this stage. The MoO_x films were grown at a substrate temperature of 120 °C in reactive O₂/Ar atmosphere at an average pressure of $p_{\text{tot}} = 0.4$ Pa. To investigate the influence of the oxygen content on the structure and properties of the deposited films, the oxygen partial pressure $p(\text{O}_2)$ during deposition was varied between 0 and 100% of the total pressure as shown in Table 1. In order to facilitate a comparison with other deposition systems with different configurations of magnetrons, pumping speeds and process gas insertion among others, the oxygen partial pressure is given relative to the total pressure in this work. The total gas pressure in the vacuum chamber during the depositions was monitored with a compact full-range gauge (Pfeiffer PKR 251). The oxygen partial pressure, however, was calculated from gas flow - pressure calibration curves obtained prior to the depositions using a hot cathode ion gauge (Leybold Ionivac) since its accuracy of $\pm 15\%$ [18] is better in the pressure range of interest than the one of the full-range gauge with approximately $\pm 30\%$ [19].

A constant direct current of 0.35 A was applied to each of the two Mo targets (diameter of 50 mm), which were mounted on magnetrons positioned opposite to the substrate holder [20,21]. The resulting discharge voltage as a function of the oxygen partial pressure is displayed in Fig. 1a. The deposition time of 30 min was kept constant. An asymmetrically bi-polar pulsed dc bias voltage with a frequency of 250 kHz and negative and positive pulse durations of 3.5 μs (−50 V) and 0.5 μs (+37 V), respectively, was applied to the substrate holder.

For analysing the microstructure of the films, cross-section as well as top-view secondary electron images were taken with a Zeiss NTS Ultra-plus SEM with an acceleration voltage between 3 and 5 kV. The chemical composition of the different MoO_x films was

Table 1

Variation of the relative oxygen partial pressure $p(\text{O}_2)$ during deposition with $p_{\text{tot}} = 0.4$ Pa.

$p(\text{O}_2)/p_{\text{tot}}$ [%]	0	28	39	48	74	90	100
Ar flow [sccm]	40	35	32	30	20	10	0
O ₂ flow [sccm]	0	5	7.5	10	20	30	40

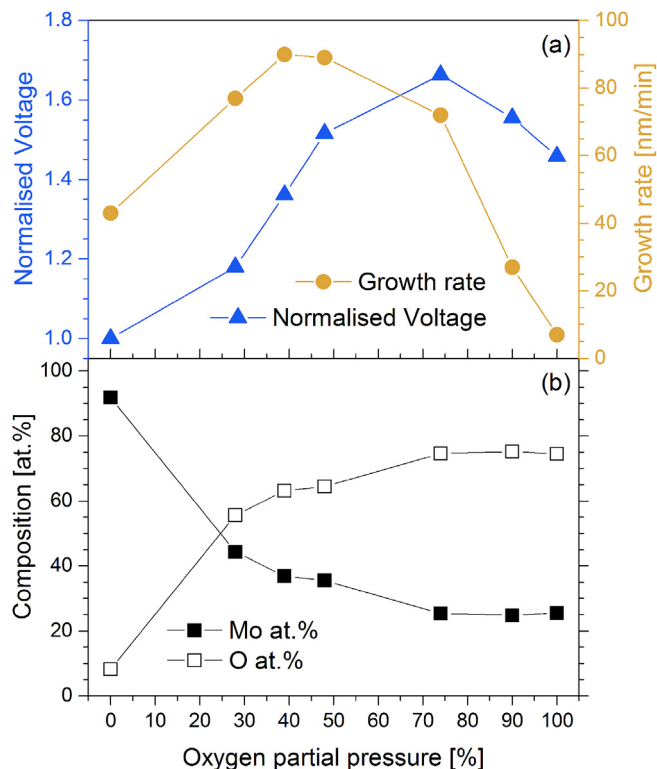


Fig. 1. a) Discharge voltage (normalised to the initial value of 305 V) and film growth rate as well as b) chemical composition of the synthesised MoO_x thin films as a function of the oxygen partial pressure.

measured by EPMA with an electron energy of 10 keV and a current of 100 nA. The identification of the crystalline oxide phases present in the films was conducted via XRD with a Bruker-AXS D8 Advance diffractometer. The measurements were done in grazing incidence mode with a fixed angle of incidence of 2° and a step of detector movement of 0.02° with an accumulation time period of 1.2 s. The diffractometer was operated at 40 mA tube current and 40 kV voltage. Cu-K_α radiation (wavelength: 0.154056 nm) and an energy-dispersive SolX detector from Bruker-AXS were used. References for phase identification were taken from the International Centre for Diffraction Data (ICDD) database [22–27]. To confirm the results of the XRD measurements, the films were also analysed by Raman spectroscopy with a HORIBA Jobin Yvon LabRam-HR800 confocal spectrometer equipped with a Nd:YAG laser (wavelength: 532.2 nm, power at the measuring spot: 3.5 mW). For qualitative analysis of the transparency, digital images of the coated glass substrates were taken. The electrical resistivity was measured by a Jandel four point probe. The biaxial stress measurements were carried out on a custom-built device using the reflection of two parallel laser beams to determine the curvature radius of the coated samples as described in Ref. [28]. The residual stress was then calculated by means of the modified Stoney's equation [29,30].

3. Results

Fig. 1 shows the evolution of the discharge voltage, the growth rate and the oxygen content in the synthesised MoO_x films depending on the oxygen partial pressure during deposition. With oxygen partial pressure increasing from 0 to 50%, the discharge voltage rose by about 50% while the film growth rate increased from ~40 to ~90 nm/min resulting in a higher film thickness (see Fig. 2) as the deposition time was kept constant. At the same time,

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