Full Length Article

Modification of molybdenum surface by low-energy oxygen implantation at room temperature

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ABSTRACT

We have studied the initial stages of oxide formation on molybdenum surfaces under $1 \, keV \, O_2^+$ ion bombardment at room temperature (RT), using x-ray photoelectron spectroscopy around Mo $3d$ or O $1s$ core-levels and the valence band photoemission. The results are compared with the oxidation mechanism of thermally oxidized Mo at RT. The thermal oxidation reveals the formation of a very thin MoO_2 layer that prevents any further adsorption of oxygen at higher oxygen doses. Oxygen implantation is more efficient in creating thicker oxide films with the simultaneous formation of several oxide compounds. The oxidation rates of MoO_2 and Mo_2O_5 follow the parabolic growth rate consistent with the mass transport driven by diffusion of either neutral or singly and doubly charged oxygen interstitials. The oxidation of MoO_3, which occurs at a later oxidation stage, follows the logarithmic rate driven by the diffusion of cations in an electric field.

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1. Introduction

Molybdenum trioxide (MoO_3) has attracted large interest over the past decade due to the specific electrical and optical properties appropriate for a variety of possible applications in different devices, ranging from the gas sensors [1] or supercapacitors [2] to the chromogenic windows [3], lithium batteries [4] or catalysts for the partial oxidation of organic molecules [5]. Therefore, much attention has been devoted to the synthesis of MoO_3 or the related heterostructured materials and nanowires, using techniques such as magnetron sputtering [6], electron beam evaporation [7], hot filament vapor deposition [8], anodic oxidation [9], pulsed laser deposition [10] or chemical vapor deposition [11]. Thermal oxidation has also been employed in order to grow the thin MoO_3 films on molybdenum metal in an oxygen environment. The Mo metal surface is quite resistant to the thermal oxidation at temperatures below 500 K [12]. For example, at room temperature (RT), oxygen adsorption saturates at about 2 monolayers [13,14], that is sufficient to prevent any further adsorption of oxygen and growth of thicker Mo oxides. Therefore, elevated temperatures are required to activate the further reaction between oxygen and Mo atoms and to provide the energy required for the atomic trans-

port [12,15,16]. Since Mo can have several oxidation states, ranging from +2 to +6, the oxidation of Mo surface usually produces several oxide compounds, the most important and commonly found being Mo(VI) oxide (MoO_3), Mo(V) oxide (Mo_2O_5) and Mo(IV) oxide (MoO_2) [13,17,18].

The thermal oxidation of many metallic surfaces starts with the dissociation of oxygen molecules from the gas phase and adsorption of separate oxygen atoms on the surface. A thin oxide layer or oxidized islands may form only if, in the next step, the adsorbed oxygen atoms exchange places with the underlying metal atoms and become incorporated below the surface [19,20]. The further growth of the oxide is then driven by the transport of metal cations, oxygen anions and/or electrons through the adsorbed layer [21–24]. At this stage, the kinetics of oxidation depends on the type of transport, which, in turn, depends on the structure and the thickness of the oxide film, the type and the number of defects or impurities or the possibility of electron tunnelling through the oxide layer [19]. Several early studies at high temperatures (above 500–600 K) revealed the parabolic rate growth for Mo oxides, that was associated with the diffusion of charged particles through the lattice defect sites (such as vacancies and interstitials known to exist within oxide films) towards the surface or the metal interface, where they react with adsorbed oxygen and form metallic oxides [15,22,25]. On the other hand, the RT oxidation of Mo produces very thin films, best described by the logarithmic rate law [26,27]. The logarithmic kinetics involves the tunnelling of electrons from metal atoms to the adsorbed O atoms at the surface. This

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process produces an electric field across the oxide, which causes the outward migration of Mo cations to the surface, or the inward migration of O anions to the oxide/metal interface [18]. The oxidation is terminated when the electric field is no longer strong enough to support the ion migration, limiting the oxide thickness to several nanometres [21,28].

It is very important to gain the information on the initial oxidation stage of Mo as it reflects the very first step of metal reaction to the oxidizing environment. However, at high temperatures, this initial reaction is very fast and it is very difficult to study all aspects of the initial oxidation stages. In the case of Mo, it implicates not only the study of the initial growth rate, but also the formation of different Mo oxides and their possible reduction or further oxidation. In the present study, we have employed x-ray photoelectron spectroscopy (XPS) in order to compare the initial stages of thermal oxidation of pure Mo metal at RT with the oxidation of the same material by the low-energy oxygen bombardment at RT. The low-energy oxygen implantation may overcome the Mo resistance to oxidation at low temperatures while introducing at the same time more lattice defect sites that promote the oxidation process. Namely, in contrast to thermal processes, the ion-induced oxidation eliminates the need for elevated temperatures and bypasses several thermally activated processes, such as adsorption, dissociation, place-exchange, diffusion or bond braking. The atomic collisions provide the decomposition of molecular oxygen into two atoms that may participate in oxidation, while, at the same time, collisions create vacancy/interstitial pairs [29] known to enhance mobility and reactivity of oxygen anions and metal cations in different materials. For example, the oxidation of Si by energetic oxygen ions is driven by the radiation-enhanced diffusion of oxygen in SiO_2 [30], while the ion-induced oxidation of Co is controlled by the diffusion of cations through the charged cation vacancies [31]. On the other hand, the irradiation of Ni with energetic electrons or ions accelerates the formation of nucleation sites for oxide formation and increases diffusivity through the radiation-enhanced diffusion of Ni in NiO [32,33]. Another advantage of implantation-induced oxidation is the possibility of controlling the composition and thickness of oxide layers, simply by tuning the energy, impact angle or the dose of impinging oxygen ions [17,31,33–35].

2. Experimental details

The molybdenum metal foil (M. Woite GmbH, 99.95 wt.% Mo) was first abraded with the SiC paper of 1200 grit and then ultrasonically cleaned with ethanol and redistilled water. Before any oxidation step, the Mo surface was additionally cleaned within the analytical ultrahigh vacuum (UHV) chamber by cycles of 5 keV Ar^+ bombardment at room temperature (these samples are referred to as cleaned samples). We have found that the annealing of the ion-cleaned surfaces at 400–500 °C for 30 min [36] did not change the XPS spectra beyond the small and expected experimental variations, with the insignificant effect on the final results provided in the present work. Therefore, in this work we present results on samples cleaned only with the Ar-ion bombardment, as done previously in some other oxidation studies of Mo [15,34,37]. The XPS survey scans on the cleaned samples have shown no carbon or argon signal and only a very small oxygen signal, corresponding to few atom% of oxygen.

Oxidation was performed in situ in the main chamber of the XPS instrument with a broad beam of 1 keV O_2^+ ions. The ion current, of typical current density of 2 μA/cm², was measured on the exit slit of the ion gun and crosschecked by the current measurements on the conductive sample holder using a Keithley multimeter. The implantation dose Φ (in O atoms/cm²) in our experiments is related to the bombardment time t (in s) as $\Phi = 1.25 \times 10^{13} t$. For
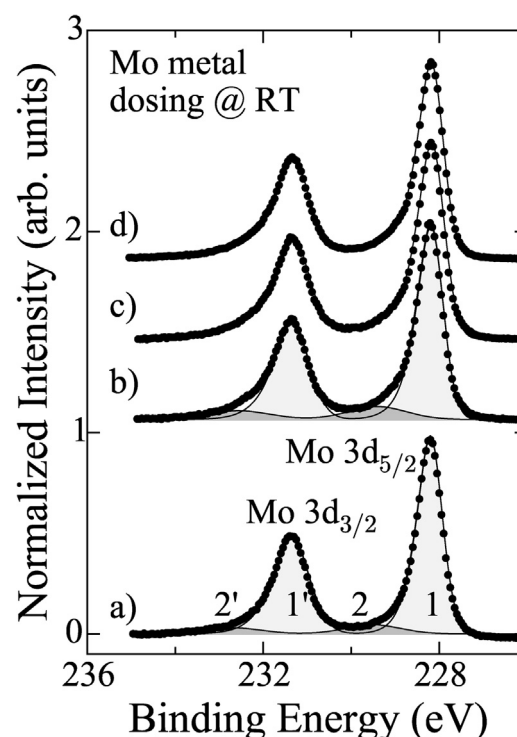
Fig. 1. Mo 3d core-level photoemission spectra (closed circles) from a cleaned molybdenum surface and surfaces oxidized at RT to 10, 50 and 5000 L of oxygen, respectively. Fitting (solid lines) represents a convolution of Gaussians and Lorentzians.

the bombardment times used in the present study (10–18000 s) the corresponding implanted dose covers more than 3 orders of magnitude, from 1.25×10^{14} to 2.25×10^{17} O atoms/cm². The thermal oxidation was performed by supplying pure oxygen gas (5.0 purity) into the UHV chamber at RT to the pressure of around 5×10^{-6} Torr. In this case, the oxidation dose is expressed in units of Langmuir, defined as $1 L = 1 \times 10^{-6}$ Torrs.

Cleaned and oxidized samples were characterized in a SPECS XPS instrument equipped with the Phoibos MCD 100 hemispherical electron analyzer and a monochromatized source of Al Kα X-rays of 1486.74 eV. For the pass energy of 10 eV, used in the present study, the resolution of the electron-energy analyzer was around 0.8 eV, as measured using the FWHM of the Ag 3$d_{5/2}$ peak from sputter-cleaned silver standard. The typical pressure in the UHV chamber during the XPS analysis was in the 10^{-9} Torr range. The photoemission spectra were simulated with several sets of mixed Gaussian-Lorentzian functions (Voigt profiles) with Shirley background subtraction using Unifit software [38] and taking into account peak asymmetries and multiplet splitting effects [12,39,40].

3. Results and discussion

3.1. Thermal oxidation of Mo at room temperature

We start the discussion with the thermal oxidation of Mo surface at RT. The formation of Mo-O bonds in different oxidation states of Mo can be determined from the chemical shifts in the XPS spectra taken around the Mo 3d core-levels. As an example, we show in Fig. 1 several Mo 3d spectra taken from the cleaned Mo surface and surfaces exposed to 10, 50 and 5000 L of oxygen at RT (closed circles in Fig. 1). Two dominant peaks (1 and 1′ in Fig. 1) are characteristic for the photoemission from the metallic Mo state (marked afterwards as Mo⁰) with the spin-orbit splitting of the Mo 3d level