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Full Length Article

# Role of surface oxidation for thickness-driven insulator-to-metal transition in epitaxial $MoO_2$ films

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ABSTRACT

Interfaces in transition metal oxides play critical roles for tuning physical properties. In thin film form, multiple interfaces can be created in between a film and a substrate, in between a film and air, and within a thin film. The role of each interface has been rarely studied. In this research, we used $MoO_2$ as a model system to study the role of the oxidized layer at film-air interface in thickness-driven metal-insulator transition. The oxidized layer at the surface is likely to be the main cause in positive temperature coefficient of resistivity in $MoO_2$ thin films thinner than about 20 nm. To find the origin of this insulating behavior in electronic transport measurements, we used x-ray diffraction, density functional theory and various spectroscopic methods. We observed the formation of oxidized $MoO_{2+x}$ at the film-air interface and its thickness explain the peculiar insulating behavior in the thinner films and even nanoparticles from the literature.

## 1. Introduction

Metal to insulator transition (MIT), colossal magneto-resistance, and electric and/or magnetic phase transitions are often found in transition metal oxides (TMOs) [1–3]. However, these phenomena have not been fully understood because of strong correlation in the oxides and complexity in chemistry. Especially, easy formation of vacancies and facile ion intercalation in some oxides make even harder to understand those phenomena experimentally. Often, these play important roles in determining the electronic and magnetic properties [4–7]. From these reasons, a lot of researches on TMOs have recently been concentrated on studying various effects of oxygen contents and their use in applications. In addition to this chemistry issue, the complex physical phenomena observed from TMOs are often explained by strain, structure, thickness etc. [8–12]. Among them, thickness sometimes drives unexpected and different properties from those of bulk materials. The role of thickness on physical properties could be the creation of strain, surface oxidation/reduction, and structural distortion [13–15]. Especially, the formation of chemically different surface layer can create natural nano-structure. One application of this complex-structured oxide system is the formation on nanocomposites for multifunctionality [16–18]. Extensive studies on nanocomposites were done to improve magnetoelectric effects, ionic conduction, and photovotaics not only in thin film form but also in core-shell structure [19–23].

Regarding the changes in physical properties and electrochemical properties by lateral nano-structure, molybdenum-containing complex oxides have been extensively studied [24–30]. Among many molybdates, metallic molybdenum dioxide ($MoO_2$) is an interesting material [31], it has metallic transport behavior, seen in Table 1, while many other rutile binary oxides show insulating behavior. Interestingly, it was reported that $MoO_2$ nano-particles with size up to 30 nm show non-metallic behavior, summarized in Table 1 [32]. The authors claimed surface oxidation would be the reason to have rather insulating behavior in the smaller nanoparticles, because the electrical ground state of $MoO_2$ is metal by formation of partially filled $t_{2g}$ band near Fermi level, [33,34] whereas $MoO_3$ is insulating. [35] Theoretically, the metallic ground state of $MoO_2$ and their electronic structure are clearly understood by Goodenough model [36]. However, so far there is no clear evidence on the effect of surface oxidation in this system.

In this work, we studied the origin of thickness-driven metal-to-insulator transition in $MoO_2$ epitaxial thin films. First, we confirmed the thickness-driven metal-to-insulator transition from electronic transport measurements. Then, we clearly probe surface oxidation is likely to be responsible for this transition. Because molybdenum oxides are a

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**Table 1**
Size dependence on transport behavior.

| | Form | Size (nm) | TCR | ρ (μOhm-cm) at 300 K |
|---|---|---|---|---|
| Roger et al. [37] | Bulk | – | Positive | 200 ~ 88 |
| Xiang et al. [32] | Nanoparticle | 30 | Negative | 200 |
| Ahn et al. [38] | Thin film | 60 | Positive | 690 |
| This work | Thin film | 9.5–19 | Negative | 4000–2400 |
| | Thin film | 38–67 | Positive | 790–420 |

promising material class for electrodes, gas sensors, and catalysts, it is expected that this finding gives critical information for developing and designing those electrochemical devices [33,39,40].

## 2. Expertimental

### 2.1. Epitaxial synthesis of $MoO_2$ thin films

Epitaxial (1 0 0) $MoO_2$ thin films were grown on thermally treated (0 0 0 1) $Al_2O_3$ substrates (Crystal Bank at Pusan National University) by RF magnetron sputtering. The details of growth condition can be found elsewhere [34]. In short, the nominal $MoO_2$ films were grown with a $MoO_3$ sintered target (Two inches in diameter). Substrate temperature and argon partial pressure ($P_{AR}$) were 500 °C and 7 mTorr, respectively. The use of Ar gas effectively reduces oxygen contents in the film. Note that (1 0 0) $MoO_2$ is stabilized on (0 0 0 1) $Al_2O_3$ with moderate anisotropic strain [34]. For studying thickness-driven metal-to-insulator transition, we used four thin films with different thickness, i.e. 9.5, 19, 38, and 67 nm.

### 2.2. X-ray scattering experiments

Thickness of each thin film was controlled by deposition time and was determined by x-ray reflectivity (XRR) using high resolution x-ray diffractometer (HRXRD, SmartLab, Rigaku). We used GenX program for XRR data analysis. In addition, we could not find any different peak other than those of (1 0 0) $MoO_2$ from the all the samples from x-ray normal scans.

### 2.3. Transport measurements

We performed a temperature dependent transport measurements with van der Pauw geometry with delta mode using a closed cycle refrigerator in a warming rate of 2 K/min. Applied current was fixed to 100 nA. Note that the indium contacts were made with conventional soldering on top of epitaxial thin films.

### 2.4. Density functional theory

Theoretical calculation was carried out using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) and the projector-augmented wave method with a plane-wave basis, as implemented in the Vienna ab initio simulation package (VASP) code [41,42]. We used a kinetic energy cutoff for plane wave of 550 eV and Γ-centered 8 × 8 × 8 k-point meshes for the Brillouin zone integration corresponding to $MoO_2$ of monoclinic phase. The structures are relaxed until the forces are less than $1 \times 10^{-3}$ eV/Å and converged in energy to $10^{-6}$ eV/cell.

### 2.5. Other spectroscopic methods

To find the possible origin of changes in electronic properties we used three spectroscopic methods. First, we used spectroscopic ellipsometry (Ellipsometer, J.A. Woollam Co., PNU-ell) to get optical conductivity. We fit optical constants of material using WVASE32 program. In this fitting process, multibeam interference and effect of substrate are also considered. Another method is x-ray absorption spectroscopy (XAS, 2A beamline, Pohang Accelerator Laboratory) with detection of total electron yield. All spectra are observed at room temperature with normal incidence. Note that the probing depth in this mode typically can reach up to 10 nm [43]. The energy range of the soft x-ray is from 525 to 550 eV to acquire oxygen *K*-edge spectra. Lastly, x-ray photoelectron spectroscopy (XPS, AXIS Supra, Kratos Analytical, PNU XPS) is used to determine the valence state of Mo 3*d* edge. The binding energy of each atom is normalized base on the binding energy of C 1s as 284.5 eV [44].

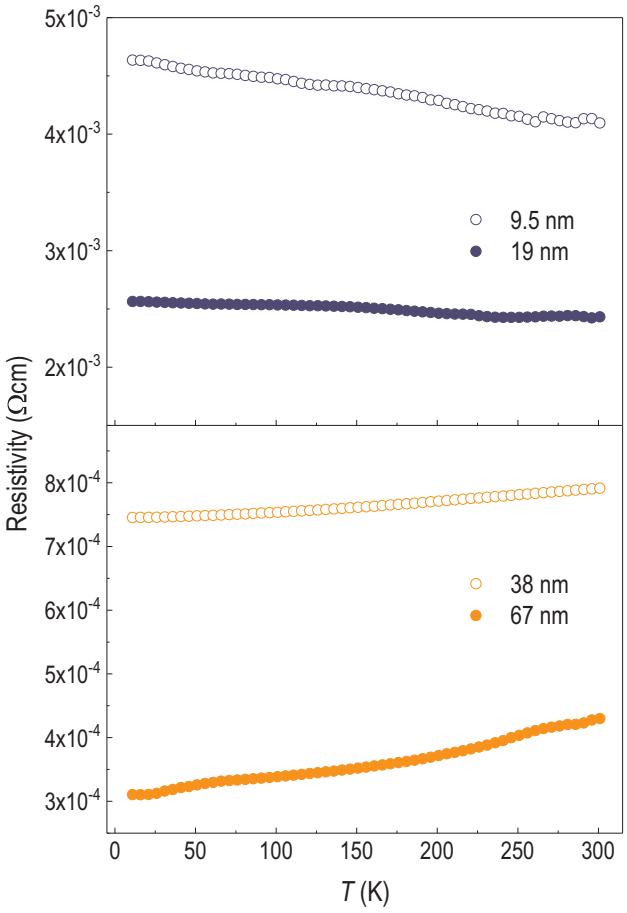


**Fig. 1.** Temperature dependent resistivity of $MoO_2$ thin films with different thickness. Negative TCR are shown under 20-nm-thick $MoO_2$.

## 3. Results and discussion

### 3.1. Thickness-driven metal-to-insulator transition

To confirm similar size-dependent insulator-to-metal transition in thin film form, we performed temperature dependent resistivity measurements, as seen in Fig. 1. From the sign of temperature coefficient of resistance (TCR), resistivity curves could be classified as two parts. The negative TCR was shown from the films thinner than 19 nm. In Fig. 1, the resistivity of 38-nm-thick and 67-nm-thick shows clear metallic behavior with positive TCR. Note that we need to emphasize that there is ten-fold increase of resistivity of the 67-nm-thick film at 300 K, which is compared with that of 9.5-nm-thick thin films. Typical temperature dependent resistivity curves can be explained by collisions between electron and phonon, and the collisions are the most dominant contribution to determine electrical resistivity of metal [45]. As an increasing temperature, the effect of thermal phonon would be accumulated. Therefore the resistivity of metal increases with temperature