

## MoO<sub>3</sub> thin film synthesis by chemical vapor transport of volatile MoO<sub>3</sub>(OH)<sub>2</sub>

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Molybdenum oxide thin films with good adhesion and crystallinity were homogeneously deposited by the chemical vapor transport of MoO<sub>3</sub>(OH)<sub>2</sub> and subsequent dehydration to the Mo oxide phase during hydrogen-reduction. This new deposition technique would be an effective deposition method for MoO<sub>3</sub> thin films due to the simple, low-cost, large area deposition and eco-friendly process. The surface morphology dramatically changed by thermal annealing at different temperatures and a uniform ~1 μm thickness was obtained. The effect of the annealing temperature is discussed.

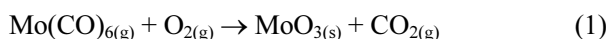
**Key words:** Molybdenum oxide, Hydrogen reduction, Chemical vapor transport, heat-treatment.

### Introduction

Molybdenum oxide (MoO<sub>3</sub>) due to its excellent optical and electronic properties, is a promising materials candidate for catalysis [1], chemical sensing [2], photochromic devices [3], electrochromic devices [4] and microbattery [5] applications.

Currently, there are several approaches to prepare MoO<sub>3</sub> thin films including sputtering [2, 6, 7], chemical vapor deposition (CVD) [8], electro-deposition [9] and evaporation [10]. Despite the development of various synthesis techniques, industrial scale deposition for applications such as smart windows [11] still remains challenging. An improvement in the deposition technique for large area chromogenic films is demanded.

In particular, chemical vapor deposition (CVD) has been regarded as a suitable technique which could induce a homogeneous thin film using vaporized phases [8]. Gesheva and Ivanova [8] successfully deposited MoO<sub>3</sub> thin films on silicon substrates by atmospheric pressure chemical vapor deposition (APCVD). The MoO<sub>3</sub> thin films found by pyrolytic decomposition of molybdenum hexacarbonyl (Mo(CO)<sub>6</sub>) vapor used as a precursor where the chemical reaction was assigned to:



On the other hand, a MoO<sub>3</sub>(OH)<sub>2(g)</sub> vapor phase was thermodynamically formed over the temperature range from 450 °C to 650 °C during the hydrogen-reduction from MoO<sub>3</sub> to MoO<sub>2</sub> [12, 13]. A volatile vapor phase (MoO<sub>3</sub>(OH)<sub>2</sub>) was transported to other particles or substrates and subsequently dehydrated to the MoO<sub>2</sub> phase. Such MoO<sub>3</sub>(OH)<sub>2</sub> can be used as a source material to deposit Mo oxide thin

films by CVD using a solid source. In this study, Mo oxide thin films were deposited by chemical vapor transport of the volatile vapor phase MoO<sub>3</sub>(OH)<sub>2</sub> and subsequent dehydration. Thermal annealing at different temperatures to evaluate the effect of the annealing temperature was conducted in an O<sub>2</sub> atmosphere and is discussed from viewpoint of changes in surface morphology.

### Experimental Procedure

MoO<sub>3</sub> powder (α-MoO<sub>3</sub>, 1-10 mm, 99.9%, JunTec) was used as the starting material for deposition of the Mo oxide thin films. An oxidized Si wafer substrate with a SiO<sub>2</sub> layer of ~500 nm thickness was washed by sonicating in acetone for 10 minutes and dried by an air blower. To deposit the Mo oxide thin films, the substrates were embedded into the MoO<sub>3</sub> powders in an Al<sub>2</sub>O<sub>3</sub> crucible and heated up to 550 °C with a heating rate of 10 K/minute which was maintained for 60 minutes in a H<sub>2</sub> atmosphere with a dew point of -76 °C. The deposited Mo oxide thin films were annealed at 500 °C and 600 °C for 60 minutes in air.

To analyze the crystalline structure of the deposited and annealed thin films, X-ray diffractometry (Rigaku RINT 2500/PC, Japan, XRD) was employed. Surface and cross sectional morphologies of the thin films were observed by a field emission scanning electron microscope (JEOL 6701F, Japan, FE-SEM). Raman spectra were acquired in the backscattering mode using a laser Raman spectrometer (JASCO NRS3100, USA) with a computer-controlled XY-stage (Prior Scientific). A 785.0 nm laser diode laser serving as the excitation source was focused onto the sample through a Olympus 100X UMPlanFL objective lens resulting in a laser spot size of ~1 μm.

### Results and Discussion

The hydrogen-reduction of Mo oxide powder takes

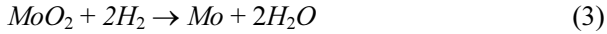
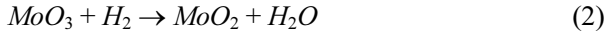
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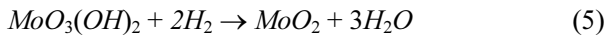
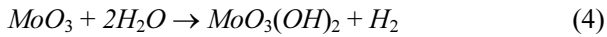
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place in two distinct stages as follows:



Reaction (2) occurs over the temperature range from 450 °C to 650 °C [14-16]. The reaction proceeds slowly yielding intermediate oxides between the trioxide and dioxides below 600 °C. As presented in Fig. 1(a), reaction (1) proceeds through two intermediate reactions involving the production of a mobile vapor phase species, (MoO<sub>3</sub>(OH)<sub>2</sub>) in the presence of water vapor.

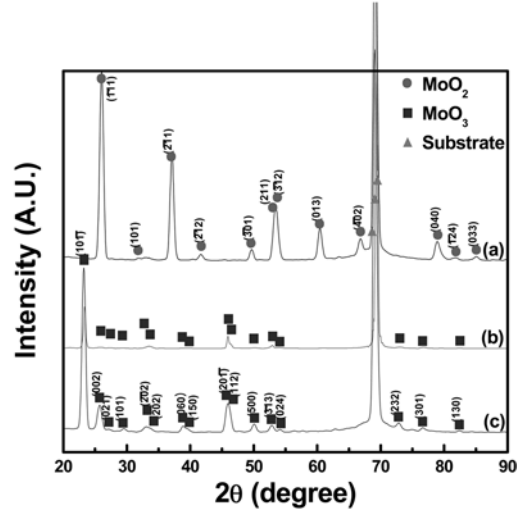


Vapor phase transport of the mobile MoO<sub>3</sub>(OH)<sub>2</sub> species to the substrate and subsequent dehydration results in the growth of a MoO<sub>2</sub> phase thin film as depicted in Fig. 1(b) [12-13]. Thus, hydrogen-reduction of MoO<sub>3</sub> powder embedding the substrate can induce a MoO<sub>2</sub> deposition on the substrate. The deposited MoO<sub>2</sub> film is subsequently annealed in an oxygen atmosphere to convert the film to the desired MoO<sub>3</sub> phase.

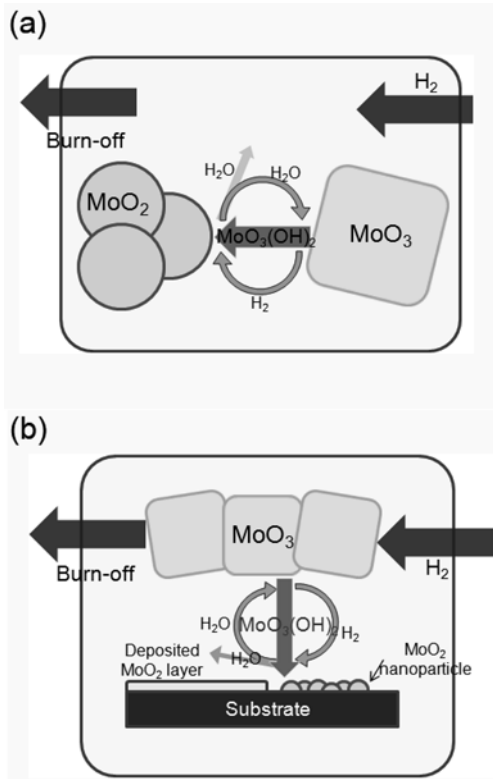
Fig. 2 shows XRD patterns of the Mo oxide thin films after deposition at 550 °C for 60 minutes in H<sub>2</sub> and subsequently annealed at 500 °C and 600 °C for 60 minutes in air. As shown in Fig. 2(a), the deposited film was mainly composed of the MoO<sub>2</sub> phase. The phase of the

deposited film changed to MoO<sub>3</sub> after annealing at 500 °C for 60 minutes (Fig. 2(b)). The crystallinity of the annealed thin film at 600 °C for 60 minutes was improved as noted in Fig. 2(c).

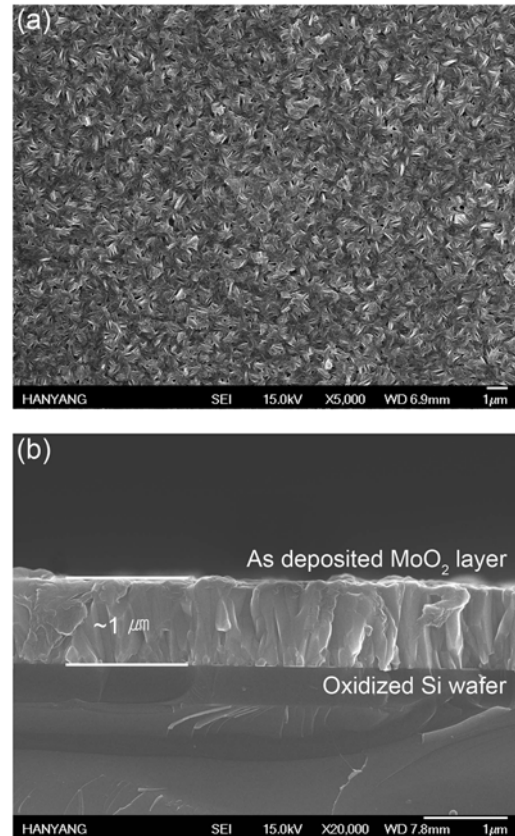
Fig. 3 shows the microstructure of as-deposited thin films. The films display a disordered needle-like morphology homogeneously covering the substrate as depicted in



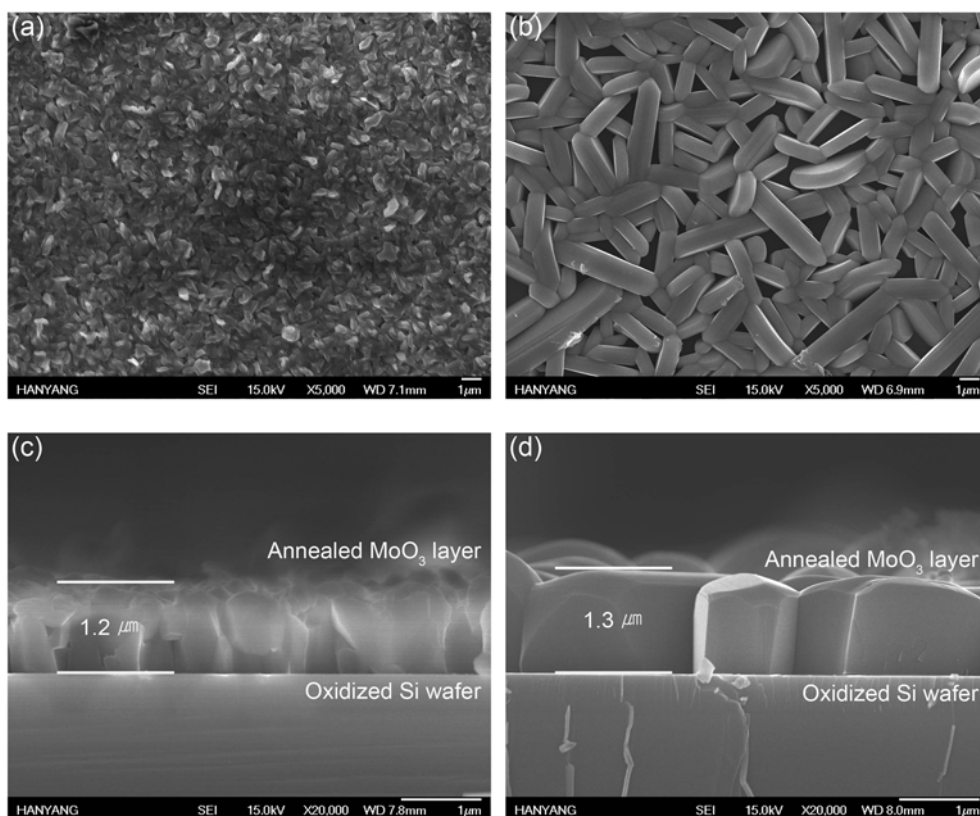
**Fig. 2.** XRD patterns of deposited Mo oxide thin films after deposition at 550 °C for 60 minutes and annealed at various temperatures in air; (a) as deposited, (b) annealed at 500 °C for 60 minutes and (c) annealed at 600 °C for 60 minutes.



**Fig. 1.** Schematic diagram of hydrogen-reduction mechanism by chemical vapor transport (CVT) to MoO<sub>2</sub> powder; (a) between powders and (b) between powder and substrate.



**Fig. 3.** Microstructures of as-deposited thin films after deposition at 550 °C for 60 minutes; (a) surface morphology and (b) cross-section.

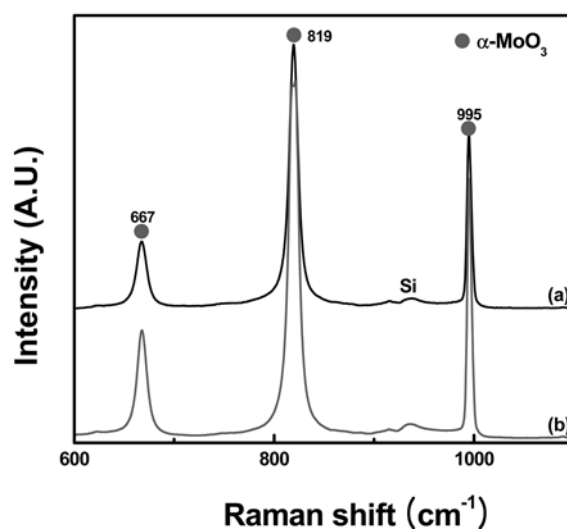


**Fig. 4.** Surface morphology and cross-sectional images of thin films deposited at 550 °C for 60 minutes annealed at various temperatures; (a),(c) 500 °C for 60 minutes and (b), (d) 600 °C for 60 minutes.

Fig. 3(a). The uniform  $\sim 1 \mu\text{m}$  thickness of the deposited thin film was obtained at a deposition rate of (Fig. 3(b)),  $\sim 0.013 \mu\text{m}/\text{minute}$ .

Fig. 4 presents the morphologies of thin films annealed at 500 °C (a,c) and 600 °C (b,d). The grains in the film became much more spherical with a change in particle size growing up to  $\sim 800 \text{ nm}$  during the annealing at 500 °C for 60 minutes. However, after annealing at 600 °C for 60 minutes, the surface morphology dramatically changed. The particle shape converted to elongated, rod-like grains with  $\sim 1 \mu\text{m}$  width and length of several micrometres as depicted in Fig. 4(b). Large scale pores are observed between  $\text{MoO}_3$  rods. This large change of morphology could be caused by enhanced crystal growth of  $\text{MoO}_3$  through diffusion. Sian and Reddy [17] discussed the effect of annealing temperature on the crystallinity in amorphous  $\text{MoO}_3$  thin films evaporated in high vacuum and reported that thermal annealing could change the state of crystallinity and confirmed this with X-ray photoelectron spectroscopy. The cross-sectional images of annealed films at 500 °C and 600 °C for 60 minutes are presented in Fig. 4(c), (d). These films exhibit good adhesion of the  $\text{MoO}_3$  film to the substrate. The thicknesses of the films annealed at 500 °C (c) and 600 °C (d) were  $\sim 1.2 \mu\text{m}$  and  $\sim 1.3 \mu\text{m}$ .

The crystal structures of the thin films annealed 500 °C and 600 °C for 60 minutes were characterized by Raman spectroscopy in (Fig. 5). Note that the peak at  $\sim 941 \text{ cm}^{-1}$  in Fig. 5(a) and (b) is from the oxidized Si wafer used



**Fig. 5.** The Raman spectra of deposited Mo oxide thin films after deposition at 550 °C for 60 minutes and annealed at various temperatures in air; (a) annealed at 500 °C for 60 minutes and (b) annealed at 600 °C for 60 minutes.

as the substrate [18]. As mentioned above, Raman spectra of two samples annealed at each temperature agreed with the results given by the XRD analysis. In the Raman spectra, the main Raman lines at 667, 819 and  $995 \text{ cm}^{-1}$  represented the stretching vibrations of the  $\alpha\text{-MoO}_3$  phase with an orthorhombic structure.  $\alpha\text{-MoO}_3$  is the stable stru-

ture compared to the metastable  $\beta$ -MoO<sub>3</sub> phase with a monoclinic structure. [19, 20] As shown in Fig. 5(a), annealing at 500 °C leads to crystallization to  $\alpha$ -MoO<sub>3</sub> and the thin film annealed at 600 °C exhibit a high degree of crystallization in agreement with the XRD results.

### Summary

In this study, homogeneous MoO<sub>2</sub> thin films of ~1  $\mu$ m thickness were accomplished with good-adhesion onto an oxidized Si wafer at 550 °C for 60 minutes by CVT of volatile MoO<sub>3</sub>(OH)<sub>2</sub> during a hydrogen-reduction of MoO<sub>3</sub> powder. A MoO<sub>3</sub> thin film was subsequently obtained by annealing of the deposited MoO<sub>2</sub> at various temperatures in air. Substantial surface morphological changes with the pores between MoO<sub>3</sub> rods occurred after annealing at 600 °C for 60 minutes. This large change of morphology was considered to arrive by enhanced crystal growth of MoO<sub>3</sub> through diffusion. The crystal structure of the thin films annealed at 500 °C and 600 °C for 60 minutes was characterized to  $\alpha$ -MoO<sub>3</sub> and the degree of crystallization was increased at the higher temperature. Such a CVT process during the hydrogen-reduction of MoO<sub>3</sub> would be an effective deposition method for MoO<sub>2</sub> thin films and a stable  $\alpha$ -MoO<sub>3</sub> phase was obtained by subsequent annealing in air.

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