Effects of Sintering Temperature on MoO\(_x\) Target and Film

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Abstract: The sintering process of the MoO\(_x\) target has an impact on the quality of the sputtered film. In this study, powders of MoO\(_3\) (78 wt\%) and MoO\(_2\) (22 wt\%) were milled and hot-pressed to prepare the MoO\(_x\) target. The effects of the sintering temperature of the MoO\(_x\) targets on the properties of the sputtered MoO\(_x\) films were investigated by X-ray diffraction, scanning electron microscopy, four-probe needle, and spectrophotometer tests. The research results revealed that the MoO\(_x\) target at the sintered temperature of 1000 \(^\circ\)C had a clear crystal structure and dense grains, exhibiting good sinterability, crystallization behavior, and film-forming property. The sputtered film deposited by the MoO\(_x\) target could obtain high quality with a smooth interface and uniform thickness. The film had smaller resistivity, higher reflectivity, and appropriate transmissivity compared to the ones fabricated by other targets that were sintered at 800 \(^\circ\)C, 900 \(^\circ\)C, and 1100 \(^\circ\)C.

Keywords: MoO\(_x\); sintering; film-forming property; microstructure

1. Introduction

Molybdenum trioxide (MoO\(_3\)), with high transparency, nontoxicity, and moderate evaporation temperature, has potential application value in the field of optoelectronic devices [1,2]. Because of a broad work function of about 6.7 eV, MoO\(_3\) can be used as the hole extraction layer in photovoltaic devices, light-emitting devices, and sensors due to photochromism, electrochromism, and low reflectance [3–5]. For these devices involving the MoO\(_x\) hole extraction layers, their capabilities mostly rely on the MoO\(_3\) thin films [6]. MoO\(_3\) is a compound-oxide semiconductor with an indirect band gap and is also considered to be a promising candidate in potential applications of hole injection layer between Transparent Conducting Oxide (TCO) and Organic Light-Emitting Diode (OLED) [7]. In the photovoltaic field, MoO\(_3\) as the cathode buffer layer can effectively improve electrode contact, lower the Schottky barrier, and then improve the photovoltaic performance of solar cells [8]. For the narrow bezel in a thin-film transistor (TFT) backplane, MoO\(_3\) is also a cost-efficient and reliable thin-film material [9]. In the new touch panel device, MoO\(_3\) can be employed as a functional film to reduce the reflection of a metal-mesh electrode and to improve the effect of shadow elimination [10]. In addition, MoO\(_3\) shows many advantages, including low cost, lightweight, and flexibility.

Molybdenum is normally oxidized with stable oxidation states of +4, +5, and +6. The Mo-O system is complex, displaying two stable oxide phases: MoO\(_2\), which is dark and opaque and is electrically conductive, and MoO\(_3\), which has a yellowish transparent appearance but is insulating [11]. Furthermore, there are numerous line phases between MoO\(_2\) and MoO\(_3\), which are brownish to greyish and are semiconducting. This complexity may be one reason for the difficulty in extracting the optical constants [12]. Magnéli [13] reported the existence of oxygen-deficient oxides (Mo\(_n\)O\(_{3n-1}\) or Mo\(_n\)O\(_{3n-2}\)). At present, the tri-oxide MoO\(_3\) film is considered the most prominent one [14]. However, MoO\(_3\) displays a poor photocatalytic property because of the wide band gap and high recombination of photo-generated electron-hole pairs [15]. Guo et al. [16] indicated that when \(x\) was smaller...
than 3, MoO$_x$ had a broader work function due to the closed shell character in the electronic structure and the dipoles created by its internal layer structure. Dominguez et al. [17] reported the good optoelectronic properties of thin MoO$_x$ films with $2 < x < 3$. Therefore, reducing the oxygen content of MoO$_3$ aims to optimize the band gap and the lifetime of electron-hole pairs [18].

MoO$_x$ film can be fabricated by reactive sputtering, pulsed laser deposition, thermal evaporation, and spin coating using molybdenum targets [19]. The process is prepared by feeding oxygen, oxygen can often improve the effectiveness of magnetron sputtering, but it is very hard to control the oxygen [20]. Lin et al. [21] used MoO$_3$ ceramic targets with a 6% O$_2$/Ar flow rate to prepare MoO$_x$ films with high transparency and an optical band gap. Hong et al. [22] manufactured MoO$_x$ nanoparticle films through laser ablation from molybdenum targets at ambient conditions. Gretener et al. [23] prepared thin MoO$_x$ films by reactive sputtering in a mixed oxygen-argon atmosphere with a metallic Mo target or a ceramic MoO$_3$ target. David et al. [24] deposited antireflection coatings to hide metal architecture by sputtering MoO$_x$ thin films. Pachlhofer et al. [11] synthesized Mo-O thin films using ceramic MoO$_x$ targets with compositions ranging from $x = 2.5$ to 2.8. To investigate the reflectance of light from external sources and the resulting color impression of the dark layer coatings, Hennrik [25] used ceramic oxide targets to deposit a thin layer of metal oxide.

In this research, MoO$_x$ ceramic target materials were prepared at different sintering temperatures through a hot-pressing sintering process, and then magnetron sputtering coating was carried out to examine the effects of different sintering temperatures on the crystal shape, microstructure, and density of MoO$_x$ ceramics, and to further compare the structure and photoelectrical properties of MoO$_x$ films. It was expected that the MoO$_x$ ceramic film as a sputtering source could be used to prepare MoO$_x$ film for the new touch panel and narrow frame LCD device based on a metal-mesh electrode.

2. Experimental Methods

Powders of MoO$_3$ (78 wt%) and MoO$_2$ (22 wt%) were ball-milled with the absolute ethanol solvent for 4 h. They were sifted and dried to obtain 50 mesh powders. The MoO$_x$ targets were prepared by hot-pressed sintering at temperatures of 800 °C, 900 °C, 1000 °C, and 1100 °C. When the sintering temperature reached the set values for 3 h, the exerting pressure was initiated. After 1.5 h, the pressure value was increased to 100 tons, and the pressure remained unchanged for 1 h. Then, the pressure and the temperature were released to the normal temperature and pressure. The hot-pressing sintered targets were achieved. Finally, the MoO$_x$ thin films were subjected to direct current (DC) sputtering in the Ar atmosphere at the power density of 2.14 W/cm$^2$ for 48 s, sodium–calcium glass was used as the substrate, and the thickness of the sputtered films was set to 45 nm. The phases of the sintered targets were identified with a DMAX-2500X x-ray diffractometry (XRD, D/MAX 2500, Rigaku, Tokyo, Japan). The morphologies of sintered targets and deposited films were observed by SEM (MIRA4 LMH, TESCAN, Brno, Czech Republic) using secondary electron imaging. The four-probe needle tester was utilized to measure the resistivity ($\rho$) of thin films, and the light transmissivity and reflectance were tested by CM-700d spectrophotometer (Konica Minolta, Tokyo, Japan).

3. Results and Discussion

Figure 1 shows the XRD patterns of the MoO$_x$ targets at different sintered temperatures. It can be observed in the samples that the existing diffraction peaks are related to the Mo$_3$O$_{11}$, MoO$_2$, Mo$_{18}$O$_{52}$, and MoO$_3$ phases. In the initial stage of sintering, the target was composed of MoO$_3$ and MoO$_2$ powders. During the sintering, the environmental atmosphere and elevated temperature resulted in non-stoichiometric and more complex
structures in MoO$_x$ targets. According to the Mo-O system calculated by Zhang et al. [26], it generates a more complex series of thermal reactions above 800 °C (Equations (1)–(4)).

$$\text{L (liquid phase)} + \text{MoO}_2 \rightarrow \text{Mo}_4\text{O}_{11} \quad (1)$$

$$\text{L (liquid phase)} + \text{Mo}_4\text{O}_{11} \rightarrow \text{Mo}_8\text{O}_{23} \quad (2)$$

$$\text{L (liquid phase)} + \text{Mo}_8\text{O}_{23} \rightarrow \text{Mo}_{18}\text{O}_{52} \quad (3)$$

$$\text{L (liquid phase)} + \text{Mo}_{18}\text{O}_{52} \rightarrow \text{MoO}_3 \quad (4)$$

Figure 1. XRD patterns of MoO$_x$ targets at different sintering temperature, (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C.

Four types of phases can be observed in MoO$_x$ targets at different sintering temperatures, but the volume fraction of phases has a significant difference due to the intensity of diffraction peaks. Moreover, the main component is the Mo$_4$O$_{11}$ phase in the sample sintered at 800 °C (Figure 1). However, the volume fraction of the Mo$_4$O$_{11}$ phase gradually decreases with an increase in the sintered temperature. When the sintered temperature increased to 900 °C, the peak intensity of MoO$_2$ increased (Figure 1b). At 1000 °C, it showed a marked variation for the Mo$_{18}$O$_{52}$ phase (Figure 1c), while the peak intensity of the MoO$_2$ exhibited no obvious change. When the sintering temperature of the MoO$_x$ target reached 1100 °C, the diffraction peaks of the MoO$_2$ phase constituted the main status (Figure 1d).

Figure 2 depicts the SEM images of the MoO$_x$ targets at different sintering temperatures, and it reveals the sintering process and grain size variation. When the sintering temperature was 800 °C, a flocculent structure was formed with crystals and loose powders (Figure 2a). The number of crystals increased at 900 °C, while that of loose powders
decreased (Figure 2b), implying a typical sintering process [27]. The bonding between powders mainly depends on the sintering temperature and diffusion rate [28]. The diffusion phenomenon can be explained using the following equation [29]:

\[ D = D_0 \exp \left( \frac{-Q}{RT} \right) \]  

(5)

where \( D \) is the diffusion coefficient, \( D_0 \) is set as a constant determined by the physicochemical property of the elements, and \( Q, R, \) and \( T \) represent the activation energy, Boltzmann’s constant, and thermodynamic temperature, respectively. Obviously, a high sintering temperature can facilitate the diffusion of the elements, creating more coalesced opportunities for powders. A dense sintered structure is dependent on a high diffusion rate; thus, the sintering temperature is recognized as the main controlling factor during the sintering process [30]. Figure 2c,d suggest that the samples sintered at 1000 °C and 1100 °C displayed a clear crystal structure. Thus, the sinterability and crystallization behavior of the MoO\(_x\) targets were improved with the increase in the sintering temperature. In addition, the density of the MoO\(_x\) targets was 4.3 g/cm\(^3\), 4.6 g/cm\(^3\), 5.6 g/cm\(^3\), and 5.1 g/cm\(^3\), respectively. This also demonstrated various sintering effects at different temperatures.

![Figure 2](image1.png)

Figure 2. SEM images of MoO\(_x\) targets at different sintering temperature, (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C.

Figure 3 depicts digital photos of the sputtered films using different MoO\(_x\) targets. According to the quality of the films, it was easy to predict the film-forming property with different MoO\(_x\) targets. When the sintering temperature of the MoO\(_x\) target was 800 °C, some spots were observed on the sputtered film (Figure 3a,b,d), presenting a ripple effect with dark specks. When the MoO\(_x\) target sintered at 1000 °C was used, a smooth
and regular surface was formed (Figure 3c). Figure 4 shows a cross-section view of the sputtered films. MoO$_x$ is a black transparent film, which is similar to a glass base, and the interface can be observed from the SEM test pictures. When the sputtering utilized an 800 °C—sintered MoO$_x$ target, the interface was very obvious, the surface morphology was rough, and the thickness of the sputtered film was 415.71 nm, which was bigger than 45 nm (Figure 4a). Although the MoO$_x$ thin film, which was prepared by the target sintered at 900 °C, displayed a smooth interface (Figure 4b), a continuous layer structure was observed on the interface, and its maximum thickness was up to 520.08 nm. The sputtered film using the 1000 °C—sintered MoO$_x$ target exhibited a uniform interface, and the thickness of the film was 44.68 nm (Figure 4c), which was very close to the set value (45 nm). Figure 4d presents a similar interface compared to Figure 4c, while a narrow peak structure is developed, which results in an asymmetric film. Thus, the 1000-°C-sintered target showed a better film-forming property compared with that of other ones. Generally, the thickness of the sputtered film is related to the distance between the target and the substrate, sputtering power, and working pressure. In this study, the technological parameters were set. By comparing the thickness uniformity of the sputtered films, the film-forming property was evaluated. Normally, the film-forming property has a close relationship with the density, grain size, and composition of the targets [4,5,22]. Thus, the inhomogeneities of MoO$_x$ led to the confusion of electromagnetic fields and the uneven distribution of plasma density. Ultimately, it resulted in the non-uniform deposition of the target atoms during the uneven sputtering process. Given the microstructure of the MoO$_x$ targets, it can be found that the MoO$_x$ target sintered at 1000 °C has a clear crystal structure with uniform grain size, indicating a good film-forming property. For the 900-°C-sintered MoO$_x$ target, the poor film-forming property was attributed to the loose structure and incomplete crystallization. The irregular film formed by the targets, which was sintered at 1100 °C, was due to the heterogeneous grain structure.

![Figure 3. Cont.](image-url)
Figure 3. Optical micrographs of MoO\textsubscript{x} targets at different sintering temperature, (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C.

Figure 4. Cross section views of sputtered films using different sintered MoO\textsubscript{x} targets, (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) 1100 °C.

Figure 5 displays the variation trend in the resistivity, reflectivity, and transmissivity of the sputtered films with the sintering temperature of MoO\textsubscript{x} targets. It was observed that the resistivity of the sputtered films was raised initially, then decreased with the increasing sintering temperature. The resistivity reflects the electrical properties of the material, which is dependent on the quality of the sputtered films \cite{11,12}. According to Figures 3 and 4, the sputtered film formed by the 800 °C—sintered MoO\textsubscript{x} target has a
rough and thick interface, which caused a high resistivity value. For the film prepared by the 900 °C—sintered MoOx target, the continuous layer structure also increased the resistivity value. However, the sputtered film using the 1000 °C—sintered MoOx target had a smaller resistivity value compared to other ones because of the smooth interface and uniform thickness. Furthermore, MoO3 presented an insulating property, and MoO2 had a better electric conductivity [11]. Thus, the sputtered film deposited by the 1100-°C-sintered MoOx target represented a smaller resistivity value compared with the ones sintered at 800 °C and 900 °C, though the narrow peak structure formed on the film. It is worth noting that the reflectivity and transmissivity of the sputtered films initially increased and then decreased with the increasing sintering temperature. It is clear that both the reflectivity and the transmissivity are controlled by the thickness and morphology of the sputtered films [17,24]. Therefore, the film, which was prepared by the targets and was sintered at 800 °C and 900 °C, presented low reflectivity and transmissivity because of its inhomogeneous structure and thick film layer. Moreover, the narrow peak structure had a great influence on the reflectivity and transmissivity of the sputtered film deposited by the 1100 °C—sintered MoOx target.

![Figure 5. Resistivity, reflectivity, and transmissivity of sputtered films deposited with MoOx targets at different sintering temperatures.](image)

4. Conclusions

The MoOx target exhibited good sinterability and crystallization behavior at 1000 °C and had a clear crystal structure, dense grains, and higher density. The MoOx target sintered at 1000 °C has a good film-forming property, which formed a smooth interface with uniform thickness, and the thickness was much closer to the set value of 45 nm. The sputtered film using the 1000 °C—sintered MoOx target had a smaller resistivity and higher reflectivity and transmittance value compared with other targets sintered at 800 °C, 900 °C, and 1100 °C. In addition, the sintered MoOx target at 1000 °C was more suitable for preparing the MoOx film of the new touch panel and the narrow frame LCD device.

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