Growth of La$_2$Mo$_2$O$_9$ films on porous Al$_2$O$_3$ substrates by radio frequency magnetron sputtering

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Abstract

Synthesis conditions of La$_2$Mo$_2$O$_9$ thin film by radio frequency (RF) sputtering technique on Al$_2$O$_3$ ceramic substrates are studied. It is found that the deposition temperature and oxygen partial pressure are the most important factors for obtaining pure La$_2$Mo$_2$O$_9$ films. Varying both parameters, Mo-rich, stoichiometric, and Mo-deficient films are obtained. With increasing the La:Mo ratio, films become denser. A crust layer is observed on top of the Mo-rich and the Mo-deficient films. The formation of the La$_2$Mo$_2$O$_9$ phase is discussed with respect to the sputtering mechanism.

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1. Introduction

Fast oxide–ion conductors keep on attracting considerable interest because of their important applications, such as solid-oxide fuel cells (SOFC), oxygen sensors and oxygen pumping devices. In SOFC applications, one limitation is the actual high operative temperature (around 1000 °C) of conventional electrolytes such as stabilized zirconias. This temperature generates correlated problems (heating cost, reactivity with electrodes, appropriate interconnection materials). The overall cost could be substantially reduced by lowering the operating temperature by 200 °C to 300 °C. For that purpose, two ways can be considered. One is to choose new material for electrolyte with enough high ionic conductivity below 800 °C. La$_2$Mo$_2$O$_9$, the parent compound of the LaMo$_x$ family of new fast oxide ion conductors, is interesting due to its high ionic conductivity of $6 \times 10^{-2}$ S cm$^{-1}$ at 800 °C [1]. It shows a phase transition between a monoclinic α-phase below 580 °C and cubic β-phase above. The oxygen–ion conductivity of the β-phase is almost 2 orders of magnitude higher than the α phase. Its high ionic conductivity at such temperature makes this material, despite its reducibility [2], potentially interesting as electrolyte in intermediate temperature SOFC [3]. The second way to lower the operating temperature is to reduce the thickness of the electrolyte layer. In principle, provided that the electrolyte film is not porous to fuel gas and oxygen, the thinner the film is, the lower the operating temperature can be. So the preparation of dense and thin LaMo$_x$ films appears to be a valuable means to achieve such a challenge. In this work, we report the preparation of La$_2$Mo$_2$O$_9$ thin films on ceramics Al$_2$O$_3$ substrates by RF-sputtering. To our knowledge, no work about La$_2$Mo$_2$O$_9$ thin films has been reported previously.

MoO$_3$ is a volatile oxide with low temperature melting point (796 °C). Moreover the La–Mo–O system shows numerous phases and polymorphism [4]. The formation of a given phase is sensitively dependent on the synthesis conditions. Prepara-

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tion of thin film of La$_2$Mo$_2$O$_9$ is challenging, because of the vaporization of Mo out of the film. Considering that the final device must operate at around 800 °C, the stability of the La$_2$Mo$_2$O$_9$ thin film at such temperatures must be checked to confirm if the film is reliable in realistic working conditions. The current work presents the in situ preparation conditions of La$_2$Mo$_2$O$_9$ thin films by magnetron sputtering with focus on the phase formation and the films microstructure.

2. Experimental details

Experiments were first started with a target of La$_2$Mo$_2$O$_9$ single phase. Films were deposited at different temperatures and oxygen partial pressures. All yielded molybdenum excess phase, irrespective of the deposition temperature or O$_2$ partial pressure. The most commonly observed phase was La$_2$Mo$_3$O$_{12}$ along with other different impurities. These results led us to change the target to La$_2$MoO$_4$ since it has an excess of La that compensates for the Mo excess deposition. Thus, a La$_2$MoO$_6$ pellet with 3 cm in diameter and 4 mm in thickness was hereafter used as the target for sputtering. In order to make the target homogeneous in composition, a wet chemical solution method termed “citrate processes” was adopted for preparation of the target. Stoichiometric La$_2$MoO$_6$ ultra fine powders were prepared by the citrate processes with La$_2$O$_3$ and (NH$_4$)$_2$-4MoO$_3$ as starting materials. The powder was pressed into pellet, which was fired at 550 °C for 6 h and then at 850 °C for 6 h and finally sintered at 1200 °C for 8 h. The obtained target was light yellow in color and very dense.

The sputtering system has already been presented elsewhere [5]. The deposition was always performed at a power density of 7 W/cm$^2$ over the target surface and at discharge frequency of 13.56 MHz. Si(100), MgAl$_2$O$_4$ (spinel), SrTiO$_3$ (peroskite) and MgO (cubic) single crystal substrates were tested as well as polycrystalline Al$_2$O$_3$. The experiments show that Si(100) substrate is not useful because of its strong reactivity with the film. Other single crystals substrates (MgAl$_2$O$_4$, SrTiO$_3$, MgO) were supposed to favour epitaxial growth because of their crystallographic symmetry close from LaMo$_x$ system. However the obtained films do not show any preferential orientation, so this kind of expensive substrates was no more justified. Instead commercial low cost alumina plates were used as substrates for the search of the optimal condition to obtain pure LaMo$_x$ polycrystalline films. The target-substrate distance was about 4 cm. The background vacuum was less than $2.6 \times 10^{-5}$ mbar. Before deposition the substrate temperature was set to the desired value for at least 20 min so that thermal equilibrium was reached in the substrate. In order to optimize the experimental conditions, deposition temperatures were varied within the range 600–750 °C and Ar/O$_2$ gas pressure was varied over a large range. The deposition time was 3 h for all samples, leading to films of approximately 1 μm thick, as measured from cross section scanning electron microscopy images of the films. After deposition, the thin films were post-annealed in situ for 10 min while maintaining the temperature and the pressure constant, after which the heating was turned off while still keeping the original ambient pressure. When the substrate temperature was less than 300 °C, the argon and oxygen ambient gas were cut off.

X-ray diffraction (XRD) measurements were performed on a Phillip’s X Pert system at room temperature. Scanning electron microscopy (SEM) measurements were carried out on a Leo 1530 VP microscope for the surface observation and cross section morphology of the films. The chemical composition was measured by Energy Dispersive X-ray analysis (EDX) using a LINK Spectrometer coupled with the SEM microscope. The transmission electron microscopy (TEM) study was performed using a JEOL 4000EX microscope (with double tilt 20°) operating at 400 keV (with a point resolution of 0.17 nm). High-resolution electron microscopy (HREM) images and selected area electron diffraction were used to study the microstructure. All HREM images were taken under defocus conditions close to Scherzer defocus (around ~55 nm). As the samples did not show any preferential orientation relative to the substrate, TEM specimens were simply prepared by gently scraping using a knife. Fourier transforms (FT) and image processing were performed using the National Institute of Health “Image” software (1.60/ppc version).

3. Results

At room temperature, La$_2$Mo$_2$O$_9$ is monoclinic [6]. However, the monoclinic distortion is very small and cannot be revealed by conventional X-ray diffraction used here. So the X-ray patterns of La$_2$Mo$_2$O$_9$ thin films in this work were indexed as a cubic phase. Nevertheless, the film purity was checked by comparison with a high-resolution pattern of a powder sample used as a standard.

3.1. Deposition temperature effect

Fig. 1 shows the XRD patterns of thin films on Al$_2$O$_3$ substrates prepared at different temperatures and at oxygen partial pressure of 6.6 Pa. In order to highlight the weak peaks, Fig. 1 is redrawn in 20 range of 24.5 – 31.5° with square root of original intensity as new y-axis scale, as shown in Fig. 2. At 600 °C, the films are a mixture of amorphous state and poor La$_2$Mo$_2$O$_9$ crystalline state. Increase of the deposition temperature enhances the crystalline quality and good crystalline La$_2$Mo$_2$O$_9$ thin films are obtained at 700 °C. Over 750 °C, two weak new peaks appears, one of which can be attributed to La$_2$MoO$_6$ as indicated with open circle, and the other which is not known as marked with #.

These results indicate that 700 °C is an ideal deposition temperature for obtaining the pure La$_2$Mo$_2$O$_9$ phase, at the argon and oxygen partial pressure we used.

3.2. Ambient gas effect

Fig. 3 shows the oxygen partial pressure dependence of the films phases at a deposition temperature of 700 °C. It is noted here that the strongest (210) peak of La$_2$Mo$_2$O$_9$ and the strongest (423) peak of La$_2$Mo$_3$O$_{12}$ phase are overlapping; both appear at a 20 angle around 27.8°. So, the second
strongest (040) peak of La$_2$Mo$_3$O$_{12}$ phase at 2θ = 29.54° is used as an indicator of the presence of this phase. It can be seen that the (040) peak exists at the oxygen partial pressure of 1.2 and 2.4 Pa, indicating that the corresponding films are a mixture of La$_2$Mo$_2$O$_9$ and La$_2$Mo$_3$O$_{12}$. With the increase of the oxygen partial pressure from 1.2 to 2.4 Pa, the intensity of the (040) peak of La$_2$Mo$_3$O$_{12}$ phase decreases. When the oxygen partial pressure is increased up to 3.3 Pa, the peak disappears completely, meaning the formation of pure La$_2$Mo$_2$O$_9$ phase within the detection limit of the XRD equipment. In order to confirm this conclusion more accurately, the XRD pattern was compared to that of standard powders, as the Fig. 3 shows, clearly indicating high agreement between the two patterns. Raman spectroscopy performed on both the film and a reference powder confirmed this conclusion (the results are not shown here). Increase of the oxygen partial pressure up to 6.5 Pa do not lead to any new phase, but enlarge the XRD peaks.

In a brief summary, the results show that, depending on the preparation conditions during sputtering, the film can be composed of (1) both La$_2$Mo$_3$O$_{12}$ and La$_2$Mo$_2$O$_9$ phases, (2) only La$_2$Mo$_2$O$_9$ phase, or (3) both La$_2$MoO$_6$ and La$_2$Mo$_2$O$_9$ phases. Considering that La:Mo is lower than 1 in La$_2$Mo$_3$O$_{12}$, equal to 1 in La$_2$Mo$_2$O$_9$ and higher than 1 in La$_2$MoO$_6$, the three kinds of films are hereafter referred as Mo-rich, stoichiometric and Mo-deficient film, respectively.

3.3. Surface morphologies

The surface morphology of a bare Al$_2$O$_3$ substrate is shown in Fig. 4.

Fig. 5a–c is the SEM images of the surface morphology of the Mo-rich (a), the stoichiometric (b) and the Mo-deficient (c) films. The three kinds of films are composed of agglomerates
of very small grains 100 nm sized. Between agglomerates are some deep fissures probably related to the substrate roughness. By comparing Figs. 5 and 4, one observes that the surface feature of all three kinds of films depends on from substrate microstructure. Namely, the conglomerations are formed on the terraces of the substrate and the fissures are formed at the hollow part between the terraces. The difference of the surface morphology between the three kinds of films is not remarkable, except that the grains in the Mo-deficient film are more rounded.

3.4. Cross sections

Fig. 5d–f shows the cross sections within an agglomerate of the Mo-rich (d), the stoichiometric (e) and the Mo-deficient films (f), respectively. All films show microstructures of mixed granular and columnar grains. From the Mo-rich, the stoichiometric to the Mo-deficient film, the film becomes denser. In the Mo-rich film, porous characteristic can even sometime be observed.

A very thin crust layer with 50 nm thickness can be observed at the top of the Mo-rich and the Mo-deficient films, as indicated by a couple of arrows in Fig. 5, while no such crust layer is observed in the stoichiometric film. It is found in the Mo-rich film that the crust layer does not cover the whole film but exists locally at the surface of the film. The part of the film underlying the crust layer seems very dense, while the part not covered with the crust layer shows porosity, as illustrated by Fig. 6. These results indicate that the formation of the crust layer is associated with the densification of the film.

3.5. TEM studies

Three electron diffraction patterns of the stoichiometric La$_2$Mo$_2$O$_9$ film along three mutually perpendicular directions are shown in Fig. 7. The most intense reflections, which form a square pattern, can be indexed in a cubic cell with lattice parameter a $\approx$ 0.72 nm (relative to the cubic cell of the high-temperature $\beta$-La$_2$Mo$_2$O$_9$), whereas the weaker ones are due to a superstructure, as observed previously on a powder sample by Goutenoire et al. [7]. Moreover, a slight monoclinic distortion of $\approx$0.5$^\circ$ was detected by electron diffraction, which is in good agreement with previous X-ray diffraction studies. HREM images along the [001] and [110] zone axis are shown in Fig. 8a and b. Fig. 8a shows a typical [001] zone image, as found in the majority of the crystals. The stacking fault or dislocation density that is usually high in oxide ceramics is very low in the present sample. The periodicity of 2a$\times$3b is confirmed with a ratio of b/a $\approx$ 1.46 that is very close to the expected one. The Fourier transform of the HREM image clearly shows extra reflections confirming that the monoclinic supercell is stable at low temperature. Fig. 8, an HREM image along [110], confirms that the c-axis is
equal to \(4a\). This result shows that the film has the same structure as the bulk \(\text{La}_2\text{Mo}_2\text{O}_9\) material.

4. Discussion

4.1. Phase formation

La–Mo–O system shows a very rich phase diagram and polymorphism, either with La-excess compounds, such as \(\text{La}_6\text{MoO}_{12}\), \(\text{La}_4\text{MoO}_9\) or \(\text{La}_2\text{MoO}_8\), etc., or with Mo-excess ones such as \(\text{La}_2\text{Mo}_7\text{O}_{12}\), \(\text{La}_2\text{Mo}_9\text{O}_{15}\), etc. It also forms compounds with ratio \(\text{La}:\text{Mo} = 1:1\), with different Mo oxidation states: \(\text{La}_2\text{Mo}_2\text{O}_9\) formed in oxidizing atmosphere (Mo\(^{6+}\)), \(\text{La}_7\text{Mo}_7\text{O}_{30}\) \([7]\) in weak reducing atmosphere (Mo\(^{5+}\), Mo\(^{6+}\)) or \(\text{La}_2\text{Mo}_2\text{O}_7\) \([8]\) in more reducing conditions (Mo\(^{4+}\)). The nature of the phase formed will depend sensitively on the La/Mo ratio in starting reactants, on the oxidizing or reducing conditions, and on the temperature at which the material is prepared. The challenge for preparation of \(\text{La}_2\text{Mo}_2\text{O}_9\) thin films is to control the La:Mo ratio to 1 during deposition.

In preparation of \(\text{La}_2\text{Mo}_2\text{O}_9\) thin films by sputtering, several mechanisms affect the composition of the film. Firstly, intrinsic factor is that Mo and La have quite different sputtering yield, which is the main factor to the nonstoichiometry of the resulting film. In our initial experiments in which \(\text{La}_2\text{Mo}_2\text{O}_9\) was used as the target, pure phase \(\text{La}_2\text{Mo}_2\text{O}_9\) was never

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Fig. 6. SEM images of the cross section at different positions at the top of the Mo-rich film. It indicates that the crust does not cover the whole film surface, but appeared locally.

Fig. 7. Electron diffraction patterns of a thin film of \(\alpha\)-\(\text{La}_2\text{Mo}_2\text{O}_9\) (a) [001]*, (b) [100]*, (c) [010]* showing the \(2 \times 3 \times 4\) superstructure.

Fig. 8. High resolution electronic microscopy image of the \(\text{La}_2\text{Mo}_2\text{O}_9\) thin film structure along the (a) [001] zone axis and (b) [110] zone axis.
obtained. EDX analysis showed that all films had molybdenum excess, irrespective of the deposition temperature or the O₂ partial pressure. The most common phase observed was La₂Mo₃O₁₂ but along with other phases. So a La-excess La₂MoO₆ target was used thereafter.

Secondly, the pressure of the argon and the oxygen processing gas has also important effects on the composition and the phase of the film, as presented in Section 3.2. Two possible mechanisms are involved.

(i) Oxygen pressure can modify the chemical state of the target surface during sputtering and therefore the sputtering yield of La and Mo. This mechanism will be especially important for Mo, because the chemical state of Mo is very sensitive to oxygen partial pressure at high temperature. In fact, the chemical reactions on the target surface during sputtering are widely observed and witnessed to play an important role in affecting the sputtering yield [9]. The fresh La₂MoO₆ target is light yellow. After being sputtered in an oxygen partial pressure of 1.2 Pa it becomes dark blue, indicating that the target surface is reduced. When the target was sputtered further in oxygen with a higher partial pressure of 3.3 Pa, the target surface turned into gray in color, indicating that Mo is partially reoxidized. The XRD diffractions were performed to check the structure changes of the target surface after they were sputtered in oxygen atmosphere of the two pressures mentioned above. Though the difference between the two pressures is small, the target surfaces show quite different XRD patterns, as shown in Fig. 9, indicating that the little difference of the oxygen partial pressure leads to quite different structures of the target surface. Accordingly, it is believed that the oxygen partial pressure plays an important role in affecting the sputtering yield in the La₂MoO₆ target.

(ii) The other effect of the sputtering atmosphere is that it causes the scattering of the La and Mo atoms during their migration from the target surface to the substrate.

Qualitatively, the lighter Mo with an atomic weight of 95.84 is more easily scattered than La with an atomic weight of 139.1. So a higher pressure of ambient gas will increase the La:Mo ratio of the film.

To sum up the effect of the partial oxygen pressure on the composition of the film, higher pressure is always favorable to increase the La:Mo ratio. Considering the very low intrinsic La:Mo ratio of the sputtering yield, a high oxygen partial pressure is therefore necessary to obtain the stoichiometric La₂Mo₂O₉ film.

Moreover, deposition temperature plays an important role in affecting the composition of the film, because the Mo is very volatile. So, high temperature leads to appearance of Mo-deficient phase. The appearance of the La₂MoO₆ phase at 750 °C can be attributed to this effect.

4.2. Microstructures

It is still difficult to understand now how the microstructures of the films are formed under different deposition conditions. A possible mechanism is proposed to interpret some observations of the film microstructures, especially the formation of the crust layer. Considering the volatility of Mo in oxides, this element will be vaporized preferably at the film surface during the sputtering and the in situ annealing. As a result, a La-rich crust layer will be formed. The formation of the crust layer will depend on the substrate temperature and the volatility of the Mo in the film. The reason why the crust layer appeared locally can be attributed to inhomogeneity of the substrate temperature, this point will be highlighted in a future work.

5. Conclusions

For the first time, La₂Mo₂O₉ thin films were prepared successfully on Al₂O₃ ceramic substrates by RF-sputtering. It is found that the deposition temperature and the oxygen partial pressure are the most important parameters in determining the phases in the as-prepared films. On varying both parameters during sputtering, three kinds of films are obtained, Mo-rich films of La₂Mo₂O₉ and La₂Mo₃O₁₂, stoichiometric films of the La₂Mo₂O₉ phase only, and Mo-deficient films of La₂Mo₂O₉ and La₂MoO₆. All three kinds of films showed very rough surface morphology. With the increase of the La:Mo ratio, the films become more dense. In the Mo-rich and the Mo-deficient film, a crust layer with thickness of about 50 nm is observed at the top of the film, while no such layer is observed in the stoichiometric film.

Concerning the mechanism which determines the composition of the film, it is proposed that the sputtering yield of Mo can be remarkably modified by the oxygen partial pressure, which determine the stoichiometry of the film.

Finally, These prototype depositions are very promising but as the aim of this work is to obtain thin films that can be used directly as electrolytes in SOFC, further depositions on conducting substrates (Ti, Pt...) are also in progress. This
work will be completed in a forthcoming paper by ionic conductivity measurement.

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