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Microstructural evolution of protective La–Cr–O films studied by transmission electron microscopy

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Abstract Transmission Electron Microscopy (TEM) and Electron Energy Loss Spectroscopy (EELS) were performed to study the microstructural evolution of La–Cr–O thin films deposited by radio frequency (RF)-magnetron sputtering on stainless steel substrates. Chromium L edges and oxygen K edges are analyzed to determine the valence states of the chromium and elucidate the phase evolution of the thin film. The as-deposited amorphous thin film crystallized to LaCrO₄ and finally transformed to the LaCrO₃ stable phase during annealing at 800 °C. An intermediate Cr/Mn oxide layer was formed in all annealed samples. The thickness of this oxide layer stabilizes after 700 °C, which indicates that the LaCrO₃ thin film plays a role in inhibiting the growth of an oxide layer on the metal surface.

Keywords Interconnect material · La–Cr–O thin films · TEM · EELS

Introduction

Cr-containing stainless steel is a promising interconnect material for high-temperature solid oxide fuel cells (SOFC) due to its cost-efficiency, high coefficient-of-thermal-

expansion (CTE) match with other SOFC components, and high reliability [1–4]. However, a metallic intermediate layer limits its application due to the low corrosive resistance and the formation of Cr-rich oxide layers. One method of protecting the metallic interconnect surface is to deposit a thin conducting oxide coating, which then acts as a barrier to prevent the oxygen from directly contacting the metallic surface [3, 5, 6]. This coating layer will also play a role in suppressing the evaporation of chromium from the metallic surface, which, otherwise, will contaminate the electrodes and lead to degradation of the SOFC performance. A LaCrO₃ perovskite thin film has been investigated recently as a promising protective coating for this purpose [7, 8].

Although there are several different methods of producing ceramic thin film coatings, radio frequency (RF) magnetron sputtering has been proved to generate well-structured LaCrO₃ thin films after annealing [4, 7]. Despite this success, however, the details of the microstructural evolution and phase transition are not yet fully understood. In our work, the as-deposited samples have been annealed at 600, 700, and 800 °C, respectively, in order to generate the different structural states of the La–Cr–O thin film that are stable at these different temperatures. (Scanning) Transmission Electron Microscopy [(S)TEM] is used to investigate the microstructure of the interfaces and thin films, and electron energy loss spectroscopy (EELS) is performed as a main tool to track the phase transformation by analyzing the valence states of chromium.

Experimental

Thin films were deposited by (RF) magnetron sputtering on Cr-containing stainless steel (SS) substrates. High-chromium ferrite Fe-23 Cr steel coupons (SS446) contain the main chemical composition of Fe (73 wt%), Cr (23 wt%), and Mn (1.5 wt%). The substrates were coated in the RF sputtering mode under 8×10^{-3} Torr Ar⁺. After pre-sputtering the target for 30 min, the substrates were moved to the position under the target. La–Cr–O film was deposited as a

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result of 5 h magnetron sputtering at 500 W of power. The deposited films were annealed at 600, 700, and 800 °C for 1 h using a controlled heating rate of 30 °C per minute, and then cooled down at the same rate as heating. Both the plain view and cross-section TEM samples were made using a standard sample preparation technique. After grinding, dimpling, and polishing, a Gatan Ar⁺ ion miller was used to thin the films to electron transparency with a 5-kV beam at an 8° incident angle. The microscope work was done in an FEI Tecnai-20 FEG TEM/STEM microscope. Electron energy loss spectra were acquired in STEM mode, with ~2 nm spatial resolution and ~0.6 eV energy resolution.

Results and discussion

Figure 1 shows the plain-view TEM images of the La–Cr–O thin films as-deposited and annealed at 600, 700, and 800 °C. The as-deposited film is structurally amorphous. A nano-structured self-assembled dendritic structure was formed after annealing, and the grain size grows with the annealing temperature. This distinctive nanostructure has been reported to have the potential application in catalysts, SOFCs, and oxygen separation membranes [9].

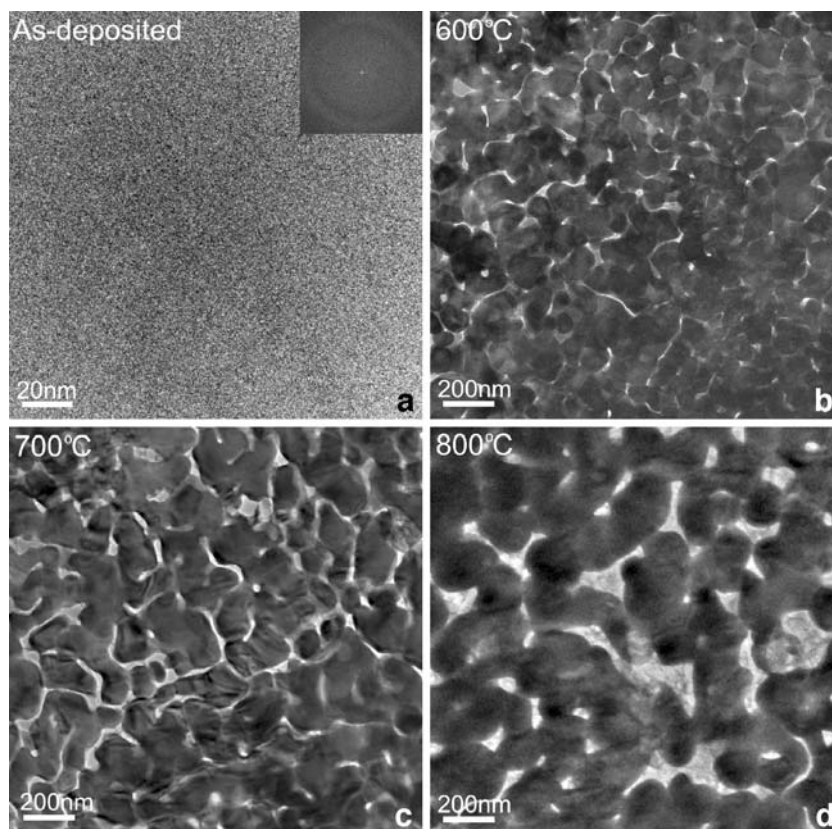
The (S)TEM study of the cross-sectional samples reveals the more detailed information on the microstructure at the interface and inside the films (Fig. 2). An intermediate layer was observed in each annealed sample. Electron energy loss spectroscopy and high-resolution TEM indicate that these intermediate layers were Mn/Cr oxides

with a nano-scale size, as shown in Fig. 3a,b. As the unoccupied oxygen 2p components are caused by the covalency between the transitional metal elements and oxygen, the characteristic oxygen K edge carries information of the transition metal elements. From the fine structure of the oxygen peak in the spectrum from the intermediate layer in Fig. 3c, the valence state of chromium in this layer can be determined to be 3+ [10]. This intermediate layer might be Cr/Mn spinel oxide due to the preferential oxidation of Mn and Cr from the alloy substrate [11].

Furthermore, since the structure and position of the chromium white lines from this intermediate layer are the same as those from the La–Cr–O film, we can expect that the valence state of chromium is also 3+ in the thin film, which means that the thin film after annealing at 800 °C is perovskite LaCrO₃. Table 1 lists the thickness of the Cr/Mn oxides layer and the thin film in each sample. There is no evidence of increasing thickness of this metal oxide layer with the annealing temperature after 700 °C (see Table 1). Moreover, the intermediate Cr/Mn oxide layer also has been investigated in a sample after annealing at 700 °C for 3 days, and no thickening was observed. This shows that the LaCrO₃ film does act as a protective coating which effectively suppresses the growth of an oxide layer on the metal surface.

The valence state of chromium in these samples was examined to study the phase evolution of the La–Cr–O thin film. By acquiring more than 40 spectra randomly on each sample, the uniform EELS spectra show that only one phase exists in those crystallized thin films, except the one

Fig. 1 TEM images of plain-view LaCrO₃ thin film samples annealed at different temperatures. The FFT image inserted in (a) indicates the amorphous nature of the as-deposited film. Self-assembled structure forms during annealing, and the grains grow larger with the increasing temperature



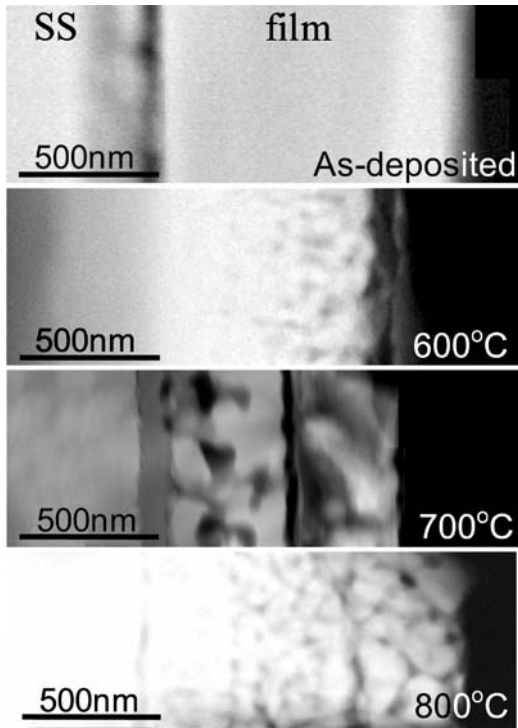


Fig. 2 Cross-section TEM images reveal in detail the microstructural evolution of the thin film

annealed at 600 °C. Typical spectra from these samples are shown in Fig. 4a, which unveil two phase transformations during annealing. The first is from as-deposited amorphous phase to crystallized phase, and the second one is from 600 to 700 °C, which is related to the valence state change in chromium.

To measure chromium oxidation state using the ratio of $L3/L2$ integrated-peak intensities, a double-step function was used for background subtraction. This method is similar to the one used by Pearson et al [12]. The Cr-

Table 1 The thickness of the thin film and the intermediate oxides layer in the samples annealed at different temperature

Annealed temperature	As deposited	600 °C	700 °C	800 °C
Thickness of Mn/Cr oxides layer (nm)	0	30	70	65
Thickness of La-Cr-O film (nm)	1,200	550	540	1,200

$L3$ pre-absorption edges was fitted with a power law and subtracted. Then, a linear function was fit to the Cr- $L2$ post edge region with a 35-eV window and extrapolated to the $L2$ maximum, which gave the first step. The other linear function formed by starting from the mid-point of the first step and with a slope the same as the one of the first linear function. This second linear function was extrapolated to reach $L3$ maximum, and forms the second step. After background subtraction, the chromium $L3$ and $L2$ peaks were integrated and the ratios of the integrations were calculated (Fig. 4b). The data are slightly higher than those reported by Daulton et al., which might be caused by using a different integration method and different microscopes [13]. At 600 °C, chromium has more than one valence state, the lowest one is 3+, because some $L3/L2$ data are the same as those from the samples annealed at 800 °C. The other possible valence states are 5+ and 6+, which need to be determined by more standard EELS work. However, according to the reported XRD results and phase transformations of powder La-Cr-O, the most likely valence state in this stage is 5+, with the phase of LaCrO_4 and 6+, as the small amount of La_2CrO_6 phase has also been detected [4, 14]. After further annealing to 700 °C, the sample turns to LaCrO_3 , according to the same $L3/L2$ value as that at 800 °C. This means that the decomposition of “ $\text{LaCrO}_4 \rightarrow \text{LaCrO}_3 + 0.5\text{O}_2$ ” happens

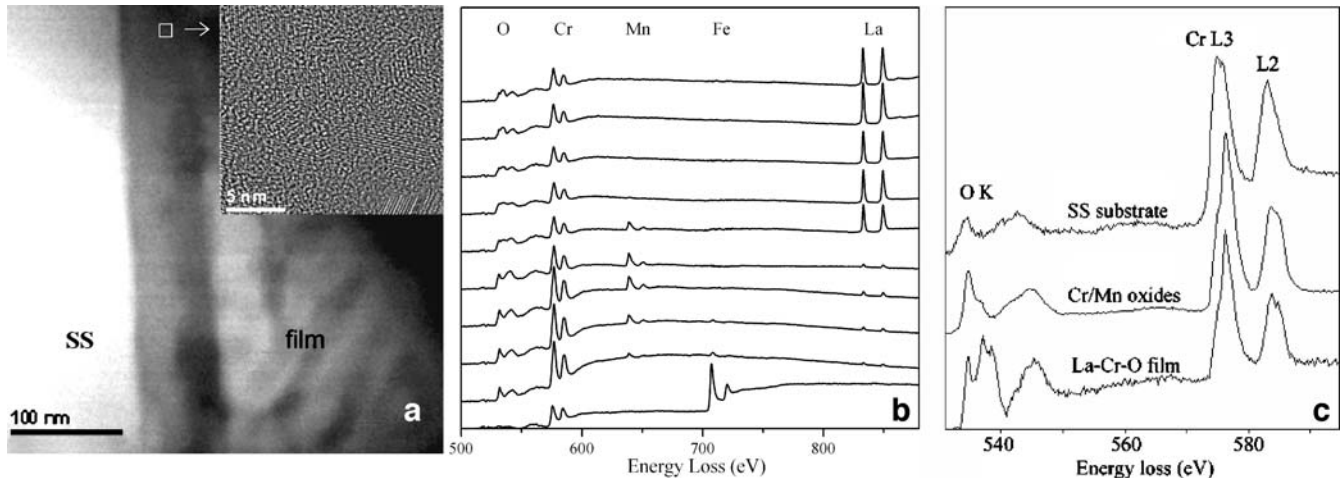


Fig. 3 a An intermediate layer exists between the substrate and the film in all annealed samples (shown here is a representative image from the sample annealed at 800 °C). The inserted high-resolution TEM image shows the oxide layer with crystallized nanograins.

b EELS shows that the intermediate layer contains Cr and Mn oxides. **c** Higher resolution EELS indicates the valence state of chromium in both oxide layer and La-Cr-O film is 3+

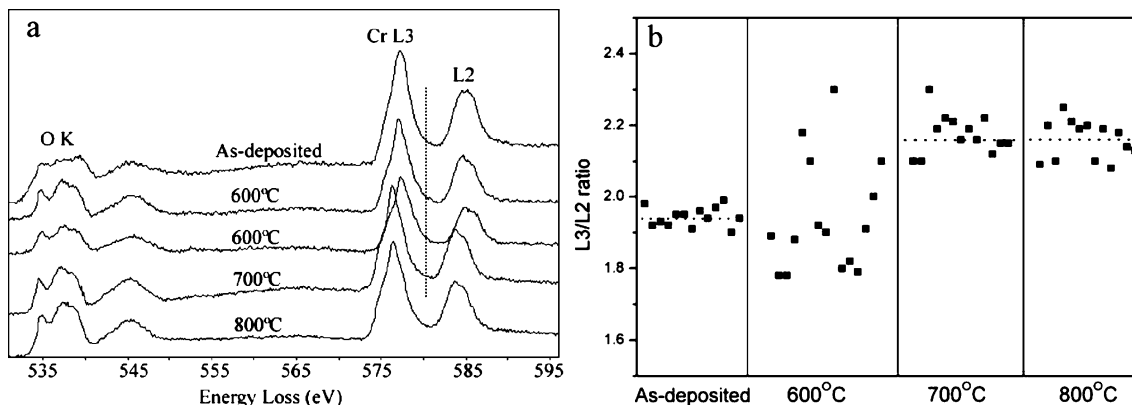


Fig. 4 The evolution of the valence state of chromium with annealing temperature displayed by edge shifting (a) and $L3/L2$ ratio (b); the dash lines in (b) show the average of the $L3/L2$ data at each temperature

at around 600 °C, which also explains the porosity increasing after 600 °C.

It should be noted that an obvious discontinuity was observed in the films, although they are prepared with a continuous deposition method (Fig. 2). The grain size and porosity alternate between different layers, which might be due to the different exposures to air in annealing. However, the different layers have the same crystal phase. The reason for this discontinuity will be explored in the future work. Therefore, we can expect to grow a LaCrO_3 thin film as dense as the inner layer in the sample annealed at 800 °C, which might be obtained by adjusting the annealing condition, in a reduced atmosphere or higher vacuum.

Conclusion

The microstructural evolution of La-Cr-O thin film deposited by RF-magnetron sputtering was investigated. EELS and (S)TEM imaging were used to study the microstructural evolution of the thin film. By tracking the valence states of chromium in the sample annealed at different temperatures, two-phase transitions have been revealed in the La-Cr-O thin film from as-deposited to 800 °C annealed: the first one is the crystallization from as-deposited amorphous phase, and the second one is from intermediate phases LaCrO_4 and La_2CrO_6 to a stable perovskite phase LaCrO_3 . The intermediate oxide layer has been proven to be Mn/Cr oxide. No evidence shows the increasing thickness of this layer, which indicates that LaCrO_3 plays a protective role in suppressing the formation of the oxide layer. On the other hand, the self-assemble microstructure of the

LaCrO_3 film shows the promising application on SOFCs, gas sensors, and other energy transformation equipment.

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References

1. Fergus JW (2005) *Mater Sci Eng A* 397:271
2. Simner SP, Anderson MD, Xia GG, Yang Z, Pederson LR, Stevenson JW (2005) *J Electrochem Soc* 152(4):A740
3. Elangovan S, Balagopal S, Timper U, Bay L, Larsen D, Hartvigsen J (2004) *J Mater Eng Perform* 13(3):265
4. Brylewski T, Nanko M, Maruyama T, Przybylski K (2001) *Solid State Ionics* 143:131
5. Orlovskaya N, Coratolo AM, Johnson C, Gemmen R (2004) *J Am Ceram Soc* 87:1981
6. Chen X, Hou PY, Jacobson CP, Visco SJ, De Jonghe LC (2005) *Solid State Ionics* 176:425
7. Zhu JH, Zhang Y, Basu A, Lu ZG, Paranthaman M, Lee DF, Payzant EA (2004) *Surf Coat Technol* 177:65
8. Johnson C, Gemmen R, Orlovskaya N (2004) *Compos Part B Eng* 35(2):167
9. Orlovskaya N, Coratolo AM, Johnson C, Gemmen R (2005) *Thin Solid Films* (in press)
10. Suzuki S, Tomita M (1997) *J Appl Phys* 36:4341
11. England DM, Virkar AV (1999) *J Electrochem Soc* 146(9):3196
12. Pearson DH, Ahn CC, Fultz B (1993) *Phys Rev B Condens Matter* 47(14):8471
13. Daulton TL, Little BJ, Lowe K, Jones-Meehan J (2001) *Microsc Microanal* 7:470
14. Azegami K, Yoshinaka M, Hirota K, Yamaguchi O (1998) *Mater Res Bull* 33:341