Effect of Thermal Cycles on Microstructure of Er₂O₃ Thin Film on SUS316 Substrate with Y₂O₃ Buffer Layer Fabricated by MOCVD Method

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Erbium oxide (Er₂O₃) and Yttrium oxide (Y₂O₃) are the promising materials to realize an advanced breeding blanket system because of good electrical resistivity and effective hydrogen permeation suppression. In this report, Er₂O₃ thin film fabricated via MOCVD process with the Y₂O₃ layer formed on SUS316 substrate before and after thermal cycles to investigate the effect of thermal cycling. Their microstructure was confirmed by SEM, AFM, TEM and STEM. The surface morphology of samples after thermal cycling has small granular structure than samples before thermal cycling and without buffer layer. According to cross sectional observation by TEM and STEM, Er₂O₃ and Y₂O₃ have different columnar structure, while buffer layer did not avoid diffusing elements from SUS316 substrate to Er₂O₃ layer. The thermal cycling test had not been affected to the growth direction of Er₂O₃ and Y₂O₃ layers, which is mostly cube-cube relationship.

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1. Introduction

In advanced breeding blanket system of nuclear fusion reactor, it needs to develop advanced type of coating to leak control of tritium and reduce Magneto Hydro-Dynamic (MHD) pressure drop¹⁾. Component materials in this system have been required to optimize conditions, for example, no breakdown at high temperature, high electrical resistivity of MHD pressure drop, and so on. Erbium oxide (Er₂O₃) coating was selected as the one of the most promising materials in ceramic coating to restrict MHD effect and tritium permeation on advanced breeding blanket system.^{1,2)} Er₂O₃ film has been formed on the surface of SUS316 steel pipe by Metal organic chemical vapor deposition (MOCVD) method by our co-worker of Hishinuma *et al.*, and its microstructure has been investigated using transmission electron microscope (TEM) in our recent work³⁾. The microstructure of Er₂O₃ column was <110>Er₂O₃ and it did not include any remarkable defects or differences before and after hydrogen permeation test⁴⁾. The thickness and width of Er₂O₃ crystalline depends on the nucleation of Er₂O₃ on SUS substrate, according to the surface condition of substrate, particularly oxide on the substrate before fabricating of film. To improve the thickness of Er₂O₃, the buffer layers have been considered about Y₂O₃ and CeO₂ buffer layers between Er₂O₃ and SUS substrate. In our recent report, Y₂O₃ with columnar structure has been formed on SUS substrate, and it makes smaller columns of Er₂O₃ than the Er₂O₃ column without buffer and with CeO₂ buffer. Er₂O₃ with buffer layer has dense structure and about 1.0 μm for thickness of Er₂O₃ and Y₂O₃⁵⁾. The crystallinity of oxide coating layer is improved by the matching of the lattice between the oxide layer and the buffer layer. There was a report that Er₂O₃ and YBa₂Cu₃O₇ crystalline grow epitaxy on Y₂O₃ layer⁶⁾.

Furthermore, it was reported that Y₂O₃ buffer layer acted effectively as the hydrogen permeation compared with CeO₂ buffer layer⁷⁾. The insulating coating is also required suitable thermal stability for practical running and an annual maintenance for 30 years at least. Our recent research has confirmed the stability of Er₂O₃ single layer fabricated on SUS 316 layer in thermal cycling⁷⁾.

In this work, Er₂O₃ film fabricated by MOCVD method on SUS316 substrate with Y₂O₃ buffer layer, and the effect of thermal stability by thermal cycle on microstructure has been investigated by XRD, AFM and TEM technique.

2. Experimental

The buffer-layer of Y₂O₃ has been formed by RF-sputtering method on a commercial SUS 316 disc plate firstly, and Er₂O₃ film has formed by metal organic chemical vapor deposition (MOCVD) process. In this work, Er₂O₃ thin film obtained via MOCVD process. Y₂O₃ buffer thin film was prepared by conventional RF sputtering method. Er(IBM)₃ (iso-butyrylpivaloylmethane) complex was used as a raw material in this process. The condition of MOCVD was already described in detail⁸⁾. The Er(IBM)₃ complex decomposes to H, C and Er clusters by thermal decomposition, and then Er₂O₃, H₂O and CO₂ are composed together with adding oxygen gas. H₂O and CO₂ gas were exhausted and Er₂O₃ was only fabricated on stainless steel 316 (SUS 316) plates. After MOCVD, sample plates were taken out from that chamber, and provided for analysis of microstructure and thermal cycling test. Scanning, transmission, scanning-transmission electron microscopes (SEM (Hitachi S3500), TEM (JEOL 4010T), STEM (JEM-2800) and atomic force microscope (AFM) (Hitachi 5100N) were used for analysis of microstructure in samples. X-ray diffraction (XRD) (Rigaku RINT2000 series) analysis with θ -2 θ scan mode was carried out with using Cu-K α X-Ray irradiation.

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Fig. 1 Overviews((a), (c)) and SEM images ((b), (d)) of samples. (a) and (b) $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ before thermal cycle, (c) and (d) $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ after 30 thermal cycles.

Small pieces of cross sectional TEM (X-TEM) sample were prepared by focused ion beam (FIB) (Hitachi FB-2100) method for TEM observation. The X-TEM samples were cut parallel to gas flow of MOCVD process. The voltage of FIB was 40 kV for Ga⁺ ion beam, and the aperture size was 520 μm in the first step, and then changed to the smallest aperture size of 15 μm for the final step. The dimension of X-TEM sample was 10 $\mu\text{m} \times 3 \mu\text{m}$, and its thickness was less than 100 nm after final thinning by FIB. A square hole was made by FIB at an interface between Er_2O_3 and Y_2O_3 before thermal cycling to obtain thinner area of X-TEM sample, and that interface has been observed by HRTEM.

3. Results and Discussions

3.1 Surface morphology of samples by SEM and AFM

Figure 1(b) and (d) are SEM images for samples in Fig. 1(a) and (c), before and after thermal cycle test. A rainbow color depending on the difference of thickness by oxide layers could be seen on the surface of each sample. White arrows in Fig. 1 correspond to the direction of gas flow in MOCVD process. White particles in Fig. 1(b) and (d) are crystalline of Er_2O_3 according to our recent work⁴⁾, and its mean size is about 170 nm in Fig. 1(b), while the mean size of particle after thermal test was smaller value of about 130 nm in Fig. (d). Figure 1(b) also shows some coarser particles, which are probably contamination during MOCVD process or aggregation of small particles around 170 nm in diameter. The mean size of 170 nm in the present work was remarkably smaller than Er_2O_3 thin film without buffer layer

reported by the previous our report. Figure 2(a) and (b) shows AFM images for samples before and after thermal cycle test. Mean distance between peaks were measured as 200 nm and 140 nm. Those values are also similar to the mean size of particles on SEM images in Fig. 1(b) and (d). Figure 3 shows XRD profiles for each sample before and after thermal cycle test. Peaks of Er_2O_3 and Y_2O_3 crystalline were detected for each sample, because the crystal structure of each oxide is the same as C-rare earth structure (space group: $Ia\bar{3}$)³⁾ and their lattice parameters are similar to each other. And each crystalline is preferentially oriented to (222) _{Er_2O_3} and (222) _{Y_2O_3} .

3.2 Er_2O_3 and Y_2O_3 buffers before thermal cycling test

Figure 4 (a) shows a X-TEM bright field images of Er_2O_3 thin film with Y_2O_3 buffer before thermal cycle prepared by FIB method. The Er_2O_3 thin film has columnar structure and it is about 620 nm for thickness before thermal cycling. Also the Y_2O_3 thin film has the narrower columnar structure about 690 nm for thickness than Er_2O_3 thin film. The difference of the cross-sectional images between two thin films was the difference of coating methods which means MOCVD for Er_2O_3 and PVD for Y_2O_3 . The selected area electron diffraction (SAED) patterns were obtained from the parts of Er_2O_3 thin film and Y_2O_3 buffer layers as Fig. 4 (b) and (c), and these incident electron beam directions were indexed as $\langle 110 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 110 \rangle_{\text{Y}_2\text{O}_3}$, respectively. $\langle 111 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Y}_2\text{O}_3}$ are mostly parallel to growth directions of each layer, although it has a deviation about 6–8 degrees. The sample was made the hole as Fig. 4 (a) using FIB technique

Fig. 2 AFM images obtained for each sample surface. (a) $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ before thermal cycle, and (b) $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ after 30 thermal cycles.

Fig. 3 XRD profiles obtained for (a) $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ before thermal cycle, and (b) $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ after 30 thermal cycles.

Fig. 4 TEM images obtained for the X-TEM sample of $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ before thermal cycle. (a) a bright field image of whole area of this sample, and SAED patterns obtained for (b) Er_2O_3 layer and (c) Y_2O_3 layer, respectively.

by low Ga^+ ion beam to obtain HRTEM image from Er_2O_3 thin film and Y_2O_3 buffer layer, respectively.

Figure 5 (a) and (c) were HRTEM images obtained for Er_2O_3 thin film and Y_2O_3 layer around the hole at points A and B in Fig. 4 (a), respectively. Figure 5 (b) and (d) were the enlarged images processed for white squares in Fig. 5 (a) and (c), and show 2 lattice spacings of about 0.30 and 0.26 nm. Those lattice spacings correspond to spacings of $\{222\}$ $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ and $\{400\}$ $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$, respectively. The direction of white arrows in Fig. 5(a) and (c) are in good agreement with $\langle 111 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Y}_2\text{O}_3}$, and those directions also correspond to growth directions of Er_2O_3 and Y_2O_3 crystalline. This result also supports to the XRD analysis in Fig. 3.

Figure 6 shows STEM images obtained for the same sample as Fig. 4 and STEM-EDS maps. Er, Y, O, Cr, Ni and Fe show homogenous distribution of these elements in each layer. It is noted that two extra layers between Y_2O_3 and SUS316 substrate can be seen in Fig. 6(a). Lines X, Y and Z were drawn in Fig. 6. There are light gray layer between lines X and Y, and brighter layer between Y and Z. According to EDS maps, Er and Y distribute upto the line Y. On the other hand, Fe achieved to the line X, and Cr and O to the line Y. This means that light gray layer between X and Y probably consist of Er, Y, Fe and O, and brighter layer between Y and Z consist of Cr, Ni and O. Those layers are maybe complex oxides which were formed during heating of MOCVD.

3.3 Effect of thermal cycles on Er_2O_3 film with buffer

As-deposited sample was provided for the thermal cycling test which is 30 times of heating-cooling sequence from room temperature to about 1023 K. Figure 7 (a) shows a X-TEM bright field image of Er_2O_3 thin film with Y_2O_3 buffer after 30 thermal cycles prepared by FIB method. The Er_2O_3 thin film has columnar structure and about 390 nm for thickness after thermal cycling, and the thickness decreased remarkably without any other damages, for example, cracking and some pores, cavities by diffusion. Y_2O_3 buffer layer had been maintained for columnar structure and the thickness during the heat cycles. SAED patterns were obtained

Fig. 5 (a) and (c) HRTEM images obtained for Er_2O_3 and Y_2O_3 layers. (b) and (d) enlarged images processed for regions marked by white squares in (a) and (c), respectively. Solid lines in Fig. 5 (b) and (d) indicate the lattice planes of $\{222\}$ $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ and $\{400\}$ $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$, respectively.

Fig. 6 (a) STEM bright field image of the sample before thermal cycles and EDS maps obtained the same area as (a). (b) Er, (c) Y, (d) O, (e) Cr, (f) Ni and (g) Fe maps.

for parts of Er_2O_3 thin film and Y_2O_3 buffer layer as Fig. 7 (b) and (c), and each incident electron beam direction was indexed as $\langle 110 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 110 \rangle_{\text{Y}_2\text{O}_3}$. $\langle 111 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Y}_2\text{O}_3}$ are mostly parallel to growth directions of each layer, although it has a deviation about 6–8 degrees. It is also the same as the result of samples without thermal cycle in Fig. 4. It means that the orientation relationship and growth direction between Er_2O_3 thin film and Y_2O_3 layer hadn't change during thermal cycles because of similarity of crystal structure and good adhesion between Er_2O_3 and Y_2O_3

layers.

Figure 8 shows that STEM image and STEM-EDS maps obtained for same sample of Fig. 7 (a). According to these maps of Fig 8, Fe, Cr, and Ni have not been detected from Er_2O_3 and Y_2O_3 layers, and these elements had not been diffused into each film during thermal cycling. Figure 8 (h) is enlarged image marked by a black rectangular in Fig. 8 (a). White dashed lines in this figure indicate the same positions at the interface. It was noted that an unknown bright region marked by an arrow, which is isolated and more grown than that in Fig. 6, exists between Y_2O_3 buffer layer and SUS316 substrate after thermal cycles. Oxygen rich layer in Fig. 8 (d) and Fe rich part in Fig. 8 (g) were corresponded to the bright region between Y_2O_3 and SUS316 substrate in Fig. 8 (h). It is suggested that complex oxides would be grown to particle shape from a thin layer during thermal cycles without extra diffusion from Er_2O_3 or Y_2O_3 layers. $\langle 111 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Y}_2\text{O}_3}$ are mostly parallel to growth directions of each layer, although they have a deviation about 6–8 degrees according to Figs. 4 and 7. For accurate analysis for SAED pattern in Fig. 4, however, the correct growth direction for Er_2O_3 and Y_2O_3 were $\langle 133 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Y}_2\text{O}_3}$, not perfect $\langle 111 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Y}_2\text{O}_3}$ on cube-cube relationship. $\langle 133 \rangle_{\text{Er}_2\text{O}_3}$ and $\langle 111 \rangle_{\text{Er}_2\text{O}_3}$ makes an angle of 12 degrees. As there is angular deviation for growth direction of Er_2O_3 because of fluctuation of gas flow during MOCVD process, which is the same as the previous report⁴⁾, we assumed that the growth direction of Er_2O_3 column in the present work is mostly equal to the cube-cube orientation relationship. The best orientation relationship for misfit is 0.51% between $\{001\}_{\text{Er}_2\text{O}_3}$ and $\{001\}_{\text{Y}_2\text{O}_3}$ of the cube-cube relationship according to the eq. (1), when the lattice parameters of 1.0548 nm and 1.0602 nm were used for Er_2O_3 and Y_2O_3 to each other⁹⁾.

Fig. 7 TEM images obtained for the X-TEM sample of $\text{Er}_2\text{O}_3/\text{Y}_2\text{O}_3$ after thermal cycle. (a) a bright field image of whole area of this sample, and SAED patterns obtained for (b) Er_2O_3 layer and (c) Y_2O_3 layer, respectively.

Fig. 8 (a) STEM bright field image of the sample after thermal cycles and EDS maps obtained the same area as (a). (b) Er, (c) Y, (d) O, (e) Cr, (f) Ni and (g) Fe maps. (h) an enlarged image marked by a black dashed rectangular in (a). White dashed lines indicate the same positions of interface.

$$\text{misfit} \frac{(hkl)_{\text{Er}_2\text{O}_3}}{(hkl)_{\text{Y}_2\text{O}_3}} [\%] = \left| \frac{d(hkl)_{\text{Er}_2\text{O}_3} - d(hkl)_{\text{Y}_2\text{O}_3}}{d(hkl)_{\text{Er}_2\text{O}_3}} \right| \times 100 \quad (1)$$

It is also suggested that the thermal cycling test do not give any effect for orientation relationship for the growth directions both of Er₂O₃ and Y₂O₃ layers.

4. Conclusions

Morphology and microstructure of Er₂O₃ thin film fabricated by MOCVD method on the SUS316 substrates with and Y₂O₃ buffer layer fabricated by RF-sputtering were investigated by some electron microscopes, XRD and AFM before and after thermal cycling test.

(1) The surface morphology of Er₂O₃ thin film was granular structure with a size of about 170–200 nm in diameter before thermal cycling test, and then it was decreased to 130–140 nm after thermal cycling test using by SEM and AFM observation.

(2) XRD peaks of Er₂O₃ and Y₂O₃ were detected for each sample before and after thermal cycles. The crystalline is preferentially oriented to (222)_{Er2O3} and (222)_{Y2O3}.

(3) The microstructure of Er₂O₃ thin film with Y₂O₃ buffer layer had not be seen any distinct damages before and after thermal cycling, although the thickness of Er₂O₃ thin film decreased from about 620 nm to about 390 nm. Fe, Cr and Ni elements in SUS316 substrate were not detected in each Er₂O₃ or Y₂O₃ layer.

(4) The results obtained for SAED and XRD analysis revealed that orientation relationship of the growth direction

for Er₂O₃ and Y₂O₃ layers had not been changed during thermal cycles.

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