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Preparation and properties of erbium oxide films deposited by radio frequency magnetron sputtering

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ABSTRACT

The erbium oxide (Er_2O_3) film is considered as a candidate for tritium permeation barrier in recent years because of its low permeation reduced ratio and easy accessibility. Erbium oxide films with different thickness were prepared by radio frequency magnetron sputtering with varying substrate temperature and sputtering time. The film surface morphology, structure, residual stress and deuterium permeation behavior were investigated. The films were compact and smooth, while the thickness varied from 200 nm to 1000 nm. The (2 2 2) preferential orientation of Er_2O_3 depressed, when the substrate temperature above 200 °C. With the substrate temperature increasing from RT to 200 °C, the compressive stress became larger, and it converted into tensile stress deposited at 400 °C. The residual stress transformed from tensile to compressive stress as the film got thicker. The permeation flux of the sample deposited with Er_2O_3 film was 2 orders of magnitude less than that of uncoated one. The permeation reduced factor (PRF) of 0.5-μm Er_2O_3 film deposited at room temperature is about 300 at 773 K.

1. Introduction

The permeation of tritium is considered as a very problematic issue in fusion power plant, which may cause environmental pollution and safety problems. The tritium permeation barrier (TPB) is the most promising solution to mitigate the radioactive tritium permeating through the steel or other metallic structural materials. Aluminum oxide (Al_2O_3) coating is widely accepted as a major candidate for tritium permeation barrier because of its high permeation reduction factor (PRF) and excellent thermal stability [1]. As its crystal constant and valence are similar to α-Al_2O_3, Er_2O_3 is proposed to be another barrier material for tritium permeation. In addition, Er_2O_3 has a good compatibility with liquid Li [2,3], and the film is more easily prepared than α-Al_2O_3 film [4–7]. Er_2O_3 also has excellent optical, electrical properties, so it has been widely studied for applications as insulator layer in CMOS devices [8,9] and antireflection coating on solar panels [10–12].

Many methods were used to prepare Er_2O_3 films, such as physical vapor deposition (PVD) [13–18], chemical vapor deposition (CVD) [19–22], atomic layer deposition [23] and the sol–gel method [1,24]. The radio frequency magnetron sputtering (RF magnetron sputtering), has a high deposition rate, low substrate temperature rise and good adhesion between the substrate and the film. Sawada [25] prepared Er_2O_3 films with high dielectric constant using RF magnetron sputtering. Er_2O_3 films with excellent morphology were fabricated by adding a SiO_2 interlayer between the film and Si substrate [3]. Er_2O_3 coating prepared by sol–gel did not present any peeling-off or crack even though it was thermally shocked for 60 cycles [1]. Several researches clarified that erbium oxide coatings show distinguished permeation reduction factors (PRF). Er_2O_3 film prepared by metal organic decomposition had PRF in the range of 10–130 [26]. The Er_2O_3 film of 0.3–1 μm prepared by physical vapor deposition yields a permeation reduction factor of 200–700. As the measurements continue, the permeation suppression efficiency degrades [27–29]. It is found that the PRF of the samples coated on both sides was one or two orders of magnitude higher than that of each side [30]. The permeation through the steel coated with μm Er_2O_3 film showed diffusion-limited regime [27].

The tritium permeation reduction factor will degrade, if the film has defects. The large residual stress is one of the most possible factors to cause crack and peeling of the film. In this paper, Er_2O_3 films were prepared on Si wafer (1 0 0) and stainless steel using RF magnetron sputtering. The film surface morphology, residual stress, structure were and deuterium permeation behavior were investigated.

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Table 1
Deposition parameters and the film properties.

Sample	Temperature (°C)	Ar flux (sccm)	Deposition time (h)	Thickness (nm)
#1	RT	40	0.5	200
#2	RT	40	1	498
#3	RT	40	2	1084
#4	200	40	1	478
#5	400	40	1	479

2. Experimental details

2.1. Sample preparation

The films were deposited using radio frequency magnetron sputtering with varying substrate temperature and deposition time. 15 mm × 5 mm rectangular silicon (1 0 0) wafer and Φ25 mm × 2 mm stainless steel samples were cleaned in acetone and alcohol by ultrasonic. Then the samples were put into the vacuum chamber, and the chamber was evacuated to 2×10^{-4} Pa before argon was introduced into the chamber at 0.5 Pa. The distance between the substrate and the target was kept at approximately 40 mm. The target was sintered Er_2O_3, with a purity of 99.9%. The substrate temperature, film thickness and residual stress are listed in Table 1.

2.2. Microstructure characterizations

The thickness was measured by Ambios XP2 step profiler, and the surface morphology was observed on a Sirion 200 field emission scanning electron microscope (FESEM) and a Shimadzu SPM 9600 atomic force microscopy (AFM). The elemental concentrations of the smooth surfaces and the particles were measured by the energy spectrum capability of the field emission scanning electron microscopy (FESEM). The structure was performed with an X'Pert PRO diffractometer by using Cu K_α radiation. The residual stress was measured by the curvature method and calculated using Stony formula on the wafer of Si (1 0 0).

2.3. Deuterium permeation experiment

The schematic view of the apparatus for deuterium permeation is shown in Fig. 1. The chamber is divided into two parts by the test sample. Both chambers are evacuated up to 10^{-6} Pa, and then deuterium (purity: 99.995%) is introduced into the coated side (called upstream) at 1.5×10^5 Pa via a leak valve. The permeation deuterium is measured using a quadruple mass spectrometer (QMS) through the sample at uncoated side (called downstream). The uncoated side is continuously pumped during the test. The permeation flux is the value when the downstream reaches equilibrium after the deuterium added into upstream. The samples are heated up to 823 K before the release of adsorbed gases. Permeation phenomena are represented by the following equation [31].

$$J = P\frac{p^n}{d} \tag{1}$$

where J is the permeation flux, P is an intrinsic parameter of a sample called permeability, p is the driving pressure introduced into the coated side, and d is the thickness of sample. The μm Er_2O_3 film coated on stainless steel showed diffusion-limited regime [27]. So the exponent n denotes permeation regime is 0.5.

3. Results and discussion

3.1. Films morphology

The surface topography of Er_2O_3 films on Si (1 0 0) wafer was observed by FESEM shown in Fig. 2. The films were smooth and uniform with only a few minute particles, and without any crack or spalling. The energy spectrum was employed to investigate the element content on the particles and the smooth surface. The content of oxygen in the particles is higher than the smooth region which was consistent to the Pint's research [32].

Fig. 3 showed the AFM images of the films deposited on Si (1 0 0) wafer at 200 °C and 400 °C. Compact and smooth surfaces were exhibited, with the size of particles below 100 nm. The root mean square roughness values increased with the substrate temperature varying from 0.669 nm for 200 °C to 1.256 nm for 400 °C compared to the range of 2–11 nm of other preparation [12]. It may be caused by the diffusion and congregation of particles at higher substrate temperature, which agrees with the previous report [33].

3.2. Structure

The crystal structure of the Er_2O_3 films on Si (1 0 0) wafer was performed by XRD. The XRD spectra were obtained in the range of diffraction angle (2θ) from 18° to 38°. Fig. 4a showed the structure of Er_2O_3 films deposited at varying temperature. The broad and predominant diffraction peak at approximate 28.7° corresponded to Er_2O_3 (2 2 2) deposited at room temperature, which indicated a preferential orientation for Er_2O_3. With the temperature increasing to 200 °C, the peak of (2 2 2) became sharp with (2 1 1) and (4 0 0) peaks appeared. The coexistence of (2 1 1), (2 2 2), (3 2 1), (4 0 0) and (4 1 1) peaks revealed no distinct preferential orientation when deposited at 400 °C. The intensity of (4 0 0) peak increased, while (2 2 2) decreased with the temperature increasing [33]. The crystalline size calculated by the Scherrer equation with the full width at the half maximum (FWHM) of the (2 2 2) diffraction peak of the Er_2O_3 films deposited at room temperature, 200 °C and 400 °C were 2.5, 11.6 and 9.0 nm, respectively.

Fig. 4b showed the XRD spectra for films with different thickness at the room temperature. When the substrate temperature kept steady, the position of XRD spectra peak remained the same while the film thickness increased, but the grain size of the films increased from 2.7 nm to 10.1 nm, which means crystallization was more sufficient.

3.3. Residual stress

The large residual stress destroys the adhesion between the film and the substrate which will lead to cracks and influence the optical, electronic properties and protective behavior of films [34]. The residual stress of the Er_2O_3 films deposited by radio frequency magnetron sputtering consists of thermal stress, intrinsic stress and extrinsic stress [35]. The thermal stress, σ, is related to the elastic strain, ε, in the film through Hooke's law.

$$\sigma = \varepsilon\frac{E_f}{1-\nu_f} = \frac{E_f(\alpha_s-\alpha_f)(T_f-T_s)}{1-\nu_f} \tag{2}$$

where E_f and ν_f are Young's modulus and Poisson's ratio of the Er_2O_3 films; α_s and α_f are the thermal expansion coefficients of the substrate and the Er_2O_3 films; T_f and T_s are the final temperature after the cooling stage and the deposition temperature. The intrinsic stress comes from the growth of particles during their condensation, migration and aggregation process which causes tensile stress [36]. The extrinsic stress includes particles bombardment through the deposition, defect and so on [37]. The particle bombardment in the stage of the deposition introduced compressive stress. The