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Er_2O_3 coating by reactive magnetron sputtering: Effect of oxygen supply and erbium pre-layer deposition

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ABSTRACT

Erbium oxide (erbia/Er_2O_3) is one of the leading candidate coating types to address the issues of tritium permeation reduction and Magnetohydrodynamic (MHD) drag reduction in fusion reactor with liquid Lead–Lithium (Pb–Li) or molten salt Flibe ($2LiF + BeF_2$) as the coolant and breeder materials. The electrical resistivity, hydrogen/deuterium permeation reduction property, liquid metal corrosion, radiation effects and deposition techniques are major areas of research on erbia coating. Though it is having a single stable phase of cubic structure up to 2300 °C, it is known to develop metastable monoclinic phase especially in sputter coating methods. We grow erbia by reactive magnetron sputter coating method and study the phase formation, electrical, microstructural and optical dielectric properties. The effects of erbium metal pre-layer deposition, post annealing in oxygen rich vacuum and oxygen to argon gas feed ratio are studied keeping other parameters constant.

The film grows in mixed phase of cubic and monoclinic structures when erbium metal pre-layer is deposited on the P91 steel substrate and in pure monoclinic phase in absence of the pre-layer. Post annealing seems to partially convert monoclinic into cubic phase in the mixed phase coating. Better crystallization and slightly more surface roughness is observed in the sample processed with higher oxygen to argon ratio. DC resistivity is found in 10^{15} Ω*cm range and it is marginally more in the sample processed with more oxygen. The spectroscopic ellipsometry on these films to obtain optical dielectric properties gives encouraging results in terms of close match of the thickness and roughness values with those obtained from SEM and AFM respectively. Systematic study of optical dielectric property suggests a trend consistent with DC resistivity.

1. Introduction

Tritium containment is extremely important in fusion fuel cycle due to the human and structural material safety issues and accountability of bred tritium, which is invaluable fuel and needs to be extracted in the most effective way. This is challenging in a blanket systems with Pb–Li eutectic and molten salt Flibe (2LiF + BeF2) breeder based designs, which is supposed to have high concentration of tritium [1]. Another issue is that of Magnetohydrodynamic (MHD) drag induced pressure drop in liquid metal flow across heavy magnetic fields [2,3]. To address these two issues of MHD drag and tritium confinement, a suitable ceramic coating on the inner surface of the volume is suggested [4].

AlN, Al_2O_3, Er_2O_3, Y_2O_3, etc., are being actively explored by the fusion materials research community world over for this purpose [5]. For Er_2O_3 coatings, substrate oxidation is one of the important factor ascribed for coating instability [6,7]. Er_2O_3 coating is deposited by various methods such as filtered vacuum arc [8], RF magnetron sputtering [9], reactive magnetron sputtering [10] metal organic decomposition [11,12] etc. Its electrical resistivity, permeation reduction factor (PRF) for hydrogen and deuterium and compatibility with liquid lithium and Pb–Li are the issues at the focus of the researchers. The resistivity is reported in the range of 10^7–10^{14} Ω*cm for measuring temperature of 800 °C to room temperature, respectively [6,13]. The PRF with erbia coating is also reported to be more than 1000, which is better than the required value [14].

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Table 1
Samples details with variation in process parameters.

O_2/Ar feed ratio	Sample-1	Sample-2	Sample-3	Sample-4
0.25	Er pre-layer, 2 h deposition @ 500 °C	Er pre-layer, 2 h deposition + 1 h annealing @ 500 °C		No Er pre-layer, 2 h deposition + 1 h annealing @ 600 °C
0.40			Er pre-layer, 2 h deposition + 1 h annealing @ 500 °C	

In this study, we deposit Er_2O_3 coating on P91 grade steel, which is very close to Reduced Activation Ferritic Martensitic Steel (RAFMS), the structural material for the blanket, in terms of structure, microstructure and composition. The crystal structure phases, electrical resistivity, surface topology, cross-sectional imaging and optical dielectric properties are studied using X-ray Diffraction (XRD), Electrometer, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Spectroscopic Ellipsometry and compared among the films deposited at varying processing conditions. Especially, the effects of oxygen supply and metallic pre-layer are studied.

2. Experimental

Reactive magnetron sputter coating of erbia on P91 grade stainless steel substrates were carried out using a 3″ planar magnetron system developed in house. The P91 steel substrates of $25 \times 25 \times 5$ mm size were mirror polished and ultrasonically cleaned in acetone before loading into the deposition chamber. In order to ensure a clean interface, the substrates were in-situ sputter cleaned prior to deposition. Substrates were kept at alleviated process temperatures (500/600 °C) during the sputter cleaning, deposition and post annealing in oxygen rich vacuum. The deposition was carried out for 2 hours. First 90 seconds, erbium pre-layer was coated by allowing the sputtering of erbium target with pure argon plasma. Subsequently, oxygen was introduced and reactive oxide coating was allowed for the rest of the time. The process was stable, consistent and reproducible with 1.0×10^{-2} mbar pressure, cathode power of 200 W and target substrate distance of about 12 cm. The process was systematically repeated to make 4 samples as listed in Table 1.

The coatings were analysed using powder mode XRD (Seifert make XRD3000PTS) with Cu Kα source, DC Electrical resistivity (Keithley make Electrometer 6517B), contact mode AFM (NT-MDT, NTEGRA), SEM at 50,000× magnification (LEO440i) and Spectroscopic Ellipsometry in 400–1100 nm range (J. A. Woollam Co).

3. Results and discussion

Having established consistency and reproducibility of the deposition experiments, we obtain highly smooth and stable coatings on P91 steel substrate, which is a close chemical analogue to Indian RAFMS, proposed to be the blanket structural material. The coatings were purple or pinkish in colour indicating the characteristic of erbia. Based on our earlier experience [10], we narrowed down to deposit on only two variants of O_2/Ar ratios, namely 0.25 and 0.4 with objective of studying growth of stable cubic phase coating at around 500 °C temperature. Another variation in the process that we report here is introduction of metallic erbium pre-layer, which may improve the stability by bridging the thermal and elastic mismatch between oxide and metallic substrate [15,16] in addition to preventing the substrate oxidation, which is a critical issue for the stability of coating [6,7]. We study the films deposited at 500 °C and 0.25 O_2/Ar ratio for the effects of post annealing in oxygen rich vacuum and then compare them with that deposited at 0.40 ratio. The powder mode XRD patterns of samples 1–3 are shown in Fig. 1 with vertical offset for clarity. The patterns clearly show that the films are consisting of cubic as well as monoclinic phases. The phase identification is performed by comparing the observed patterns with JCPDS standard pattern of cubic phase [17] and simulated pattern of monoclinic phase [10]. Cubic phase of erbium oxide is thermally stable up to 2300 °C whereas monoclinic is a metastable phase that can form under high pressure. Sputter coated films are inherently residually stressed and this may stimulate formation of monoclinic phase as reported earlier [10]. Though there are strong overlaps among the peaks of cubic and monoclinic phases, fortunately there is one unique peak from each phase. The peak at ~20.60° is a clean (2 1 1) peak of cubic phase and one at 26.75° is of monoclinic phase. Moreover, (2 2 2) cubic peak at 29.27° and partially overlapping bunch of monoclinic peaks extending up to 30.53° also show significant evidence to help us distinguish the two phases. Close observation reveals that sample-1 consists of dominantly monoclinic phase, whereas contribution from cubic phase dominates in sample-2. This suggests that post annealing for 1 h is significantly transforming the metastable phase into cubic phase, but not completely. However, post annealing on sample-3 processed with higher oxygen availability is relatively less effective in increasing the cubic phase content any more. The clean monoclinic peak of sample-1 (26.26°) is shifted to lower angle as compared to positions of simulated room temperature monoclinic phase (26.75°) and the shift gets systematically reduced for sample-2 (26.54°) and sample-3 (26.68°) indicating that post annealing and higher oxygen availability reduces the compressive residual stress in this phase. On the other hand, cubic (2 2 2) peak at ~29° is nearly unchanged and is slightly at lower angle as compared to the normal position (29.27°), indicating that the cubic phase is also under compressive stress and it is not changing significantly with this variations of process.

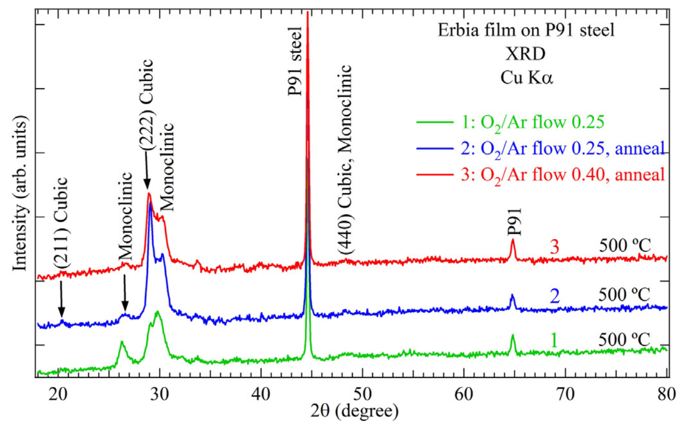

Fig. 1. XRD patterns of sample-1, 2 and 3 with constant relative vertical offset.

Furthermore, we analyse the surface topology and microstructure using atomic force microscopy on sample-2 and sample-3 to study the effect of higher oxygen availability at 500°C processing temperature. Fig. 2 shows the AFM images of the two samples on 3×3 µm area. Relative study indicates that more oxygen in sample-3 processing leads to larger crystallites of upto about