Nuclear Materials and Energy 10 (2017) 1–8

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

# The influence of annealing on yttrium oxide thin film deposited by reactive magnetron sputtering: Process and microstructure

Y. Mao*, J. Engels, A. Houben, M. Rasinski, J. Steffens, A. Terra, Ch. Linsmeier, J.W. Coenen

*Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik, Partner in the Trilateral Euregio Cluster, 52425 Jülich, Germany*

ARTICLE INFO

*Article history:*
Received 12 September 2016
Available online 26 January 2017

*Keywords:*
Yttrium oxide
Reactive magnetron sputtering
Annealing
Microstructure
Permeation barrier
Composite interface

ABSTRACT

Yttrium oxide thin films were prepared by reactive magnetron sputtering in different deposition condition with various oxygen flow rates. The annealing influence on the yttrium oxide film microstructure is investigated. The oxygen flow shows a hysteresis behavior on the deposition rate. With a low oxygen flow rate, the so called metallic mode process with a high deposition rate (up to 1.4 µm/h) was achieved, while with a high oxygen flow rate, the process was considered to be in the poisoned mode with an extremely low deposition rate (around 20 nm/h). X-ray diffraction (XRD) results show that the yttrium oxide films that were produced in the metallic mode represent a mixture of different crystal structures including the metastable monoclinic phase and the stable cubic phase, while the poisoned mode products show a dominating monoclinic phase. The thin films prepared in metallic mode have relatively dense structures with less porosity. Annealing at 600 °C for 15 h, as a structure stabilizing process, caused a phase transformation that changes the metastable monoclinic phase to stable cubic phase for both poisoned mode and metallic mode. The composition of yttrium oxide thin films changed from nonstoichiometric to stoichiometric together with a lattice parameter variation during annealing process. For the metallic mode deposition however, cracks were formed due to the thermal expansion coefficient difference between thin film and the substrate material which was not seen in poisoned mode deposition. The yttrium oxide thin films that deposited in different modes give various application options as a nuclear material.



## 1. Introduction

Yttrium oxide is an industrially and technologically very useful ceramic material under its several advanced properties: good thermal and chemical stability, high mechanical strength and hardness [1-3]. Also yttrium oxide has a wide application in nuclear research because of its low activation due to neutron irradiation [4].

Yttrium oxide exhibits several structural polymorphisms: C-cubic (Ia3), B-monoclinic (C2/m), A-hexagonal (P32m) and H-hexagonal ($P6_3/mmc$). The cubic phase is stable at room temperature, which transforms to H-hexagonal phase at ~2327 °C or to B-monoclinic phase at ~10 GPa [5-8]. Therefore, in low temperature region (<2327 °C), the cubic phase, as the stable phase, is normally preferred.

One option for producing the yttrium oxide thin film is to use reactive magnetron sputtering deposition. Using the reactive magnetron sputtering process to produce compound material has been well investigated, especially the influence of the amount of the reactive gas on the deposition process and thin film properties [9-12]. In reactive magnetron sputtering of yttrium oxide, a hysteresis of the deposition parameters as a function of the oxygen flow is often reported. At low oxygen flow the deposition rate is quite high, and therefore only little yttrium oxide compound is formed on the target and this regime is referred to as the metallic mode. At high oxygen flow the target becomes more oxidized, and the deposition rate decreases. This regime is called the poisoned mode.

Recent research by Lei et al. [12] demonstrated that, for yttrium oxide deposition, metallic mode and poisoned mode give different phases, which are the cubic phase and the monoclinic phase, respectively. Comparing to poisoned mode thin films, the yttrium oxide coatings deposited in metallic mode have a relatively dense structure, less porosity and larger grain size and are considered a preferred coating due to their superior mechanical properties. Nevertheless, this conclusion still needs to be confirmed for nuclear application (high temperature application), for which the annealing becomes a necessary post treatment for the sputtered yttrium oxide thin film to reach the stable structure. Therefore this work

* Corresponding author.
*E-mail address:* y.mao@fz-juelich.de (Y. Mao).

http://dx.doi.org/10.1016/j.nme.2016.12.031

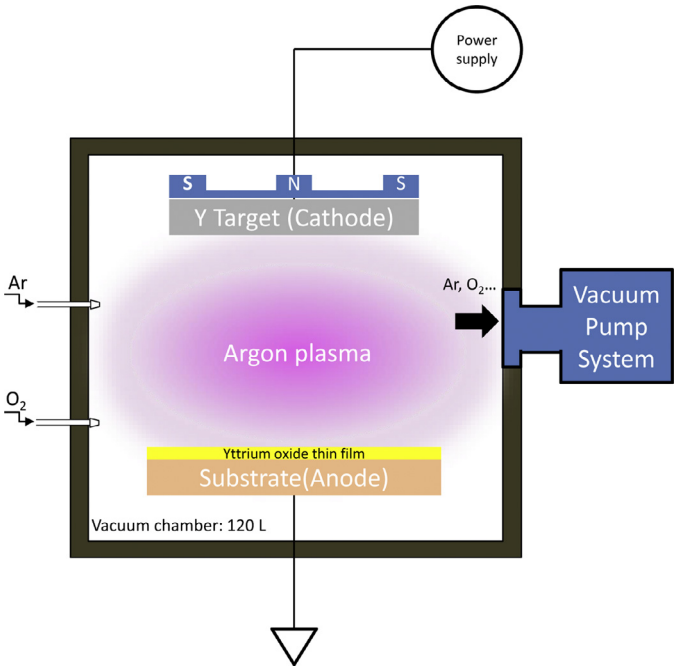


**Fig. 1.** The magnetron sputtering setup.

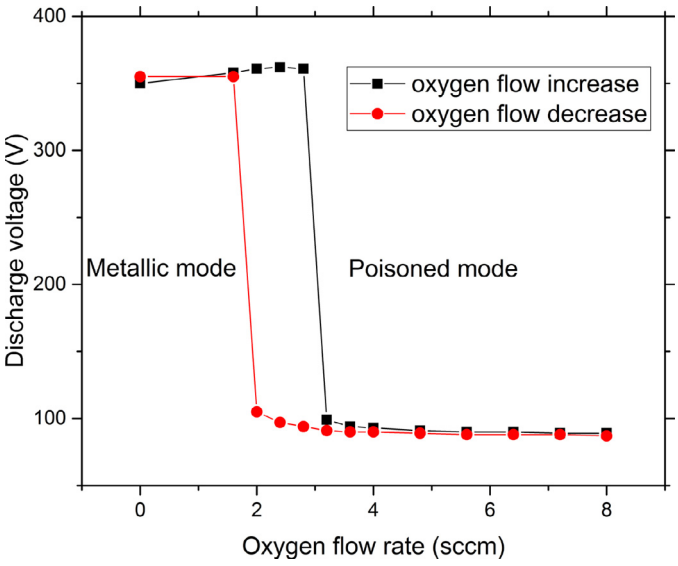


**Fig. 2.** Oxygen flow influence on discharge voltage at 350 W RF power supply.

investigates further the post-annealing influence on the reactive magnetron sputtered yttrium oxide thin film microstructure.

## 2. Experimental techniques

### 2.1. Deposition and annealing

The yttrium oxide thin films were deposited by a Prevac magnetron sputtering system (Fig. 1) on the polished P92 steel (0.07%–0.13% C; 0.3%–0.6% Mn; max 0.02% P; max 0.01% S; max 0.5% Si; 8.5%–9.5% Cr; 0.3%–0.6% Mo; 0.15%–0.25% V; 0.03%–0.07% N; max 0.4% Ni; max 0.02% Al; 0.04%–0.09% Nb; 1.5%–2% W; 0.001–0.006% B; max 0.01% Ti; max 0.01% Zr) substrates with the microstructure of martensite. It is a substitute for the potential fusion reactor structural material, EUROFER. The magnetron target material was yttrium metal (Kurt J. Lesker Company, 99.9% purity, 76.2 mm diameter, 6.35 mm thickness). The distance between the target and the substrate is ~15 cm. Argon was used to generate the plasma. Oxygen was injected as reactive gas, so that yttrium oxide compound could be formed. The oxygen inlet position was away from the target, around the sample stage. An RF power supply with 13.45 MHz frequency was used to avoid the arcing effect of DC power supply [9,13]. The deposition power was 350 W. In a single deposition process several substrates were placed on the sample stage, which rotated with a speed of 20 °/s during the deposition process to guarantee the homogeneous distribution of the deposition. The substrate temperature during deposition was about 140 °C due primarily to the kinetic energy and heat of condensation of coating atoms and plasma radiation. The oxygen flow changed between 2 standard cubic centimeter per minute (sccm) and 10 sccm measured by a gas flow controller. The Ar flow rate was constant 25 sccm in all cases. The vacuum chamber background pressure was $\sim 5 \times 10^{-8}$ mbar and the pressure during deposition was $\sim 6.5 \times 10^{-3}$ mbar. The pumping speed was 212 L/s.

After deposition, some samples were annealed at 600 °C for 15 h by using a vacuum tube furnace. The pressure in the vacuum tube furnace during annealing was $\sim 1 \times 10^{-5}$ mbar. The average heating rate and cooling rate were ~4 °C/min and ~1.7 °C/min, respectively.

### 2.2. Characterization

To calculate the deposition rate of each process, the exact yttrium oxide film thickness after deposition was measured by using a Dektak 6 M profilometer. The microstructure of the films was analyzed by a dual beam SEM/FIB (focused ion beam) Carl Zeiss Crossbeam 540 device together with an energy-dispersive X-ray spectroscopy (EDX). A glow discharge optical emission spectroscopy (GD-OES, RF mode with 1.011 kHz frequency and a duty cycle of 0.1, 800 V bias voltage, 3.72 mbar plasma pressure) was utilized to quantitatively measure the thin film composition [14]. Crystallographic properties were measured by a D8 Discovery X-ray Diffractometer (XRD) using Cu-K$\alpha$ radiation (0.154 nm) in Bragg–Brentano geometry with a $2\theta$ range from 10° to 60°

## 3. Results and discussion

### 3.1. Deposition condition and deposition rate

Fig. 2 illustrates the relationship between discharge voltage and the oxygen flow at 350 W RF power supply. This diagram shows a hysteresis behavior as many papers have reported about reactive magnetron sputtering [11-13,15]. When the oxygen flux increases, the discharge voltage firstly remains at a high value over 300 V. When the oxygen flow reaches about 3 sccm, the deposition voltage abruptly drops to a low point, and then remains relatively constant at the low value below 100 V with the further increasing of oxygen flow rate. When the oxygen flux decreases from 8 sccm, firstly the discharge voltage remains at the low value. After the oxygen flow rate decreases to about 2 sccm, the deposition voltage suddenly increases to the high value again, and then remains relatively constant when the oxygen flow rate further decreases.

The high and low discharge voltages correspond to different deposition mechanisms which are the so called metallic mode and poisoned mode, respectively. In metallic mode, mainly the yttrium metal atoms are sputtered from the target, and impinge on the substrate with a reaction with the inject oxygen forming an yttrium oxide thin film. However, during poisoned mode deposition with a high oxygen flux, the increasing excess oxygen can diffuse up to the yttrium metal target forming an yttrium oxide compound layer on the target surface. Sputtering rates from compound targets are less than that of pure metallic target by a factor up to 50 [12]. There are two main reasons: a) the sputtering yield of metal atoms