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The effect of substrate temperature on the oxidation behavior of erbium thick films

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ABSTRACT

The effect of substrate temperature on the oxidation behavior of erbium thick films, fabricated by electron-beam vapor deposition (EBVD), was investigated by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The erbium thick film is black when it is deposited at substrate temperature below 450 °C and turns gray at higher substrate temperature in a vacuum pressure of approximately 1.5×10^{-6} Torr, which indicates that the thickness of erbium oxide layer formed on the surface of erbium films increases with the decreasing substrate temperature. XPS depth profile results demonstrate that the thickness of the surface erbium oxide layer of erbium film deposited at substrate temperature of 550 and 350 °C are about 50 and 75 nm, respectively. The thicker oxide layer at lower substrate temperatures may be attributed to grain size and the dynamic vacuum condition around the substrates. Other possible factors involved in the oxidation behavior are also discussed.

1. Introduction

Films of erbium, a rare earth metal, with thickness of 3–6 μm is under consideration to be a candidate material as tritium (T) target of neutron generator (NG) [1]. The critical reasons are because of the property of long time storage in solid phase of its hydride [2], as well as excellent thermal stability of tritium [3] and helium (He) [4] generated by the decay of T in the Er-T-He ternary system. Systematic research on erbium films has been employed for its potential application in the nuclear industry. The erbium oxide layer, formed on the surface of erbium film due to its high susceptibility to oxidation in the deposition process, degrades the thermal dynamic properties for absorbing T by inhibiting T diffusion into the film to react with erbium. Brumbach et al. found that the thermal annealing either with higher temperature or with longer annealing times leads to a degradation of the passive oxide leading to a bulk film more accessible for hydrogen loading [5]. Holloway reported that the electron-beam deposited erbium films had surface oxide layer with thickness ranged from 17 to 19 nm after exposure to air, whereas the hydrided erbium films had oxide thickness of 11–35 nm after annealing at temperatures up to 500 °C in a ambient at 1.0×10^{-8} Torr [6]. Parish et al. demonstrated that the erbium oxide formation would proceed readily during processing, which may detrimentally contaminate $Er(H,D,T)_2$ films [7]. An additional platinum layer deposited on erbium surface immediately after erbium deposition without air exposure between deposition steps was employed to avoid the formation of erbium oxide compound and improve the capacity of absorbing T [8].

Generally, high temperature annealing would enhance the level of oxidation of metal bulk and film specimens due to their stronger reactivity at high temperature. Thermal oxidation induces a surface smoothening of Ti–Ni thin films and surface roughness of oxidized Ti–Ni films decreases with the increasing oxidation temperature [9]. Roberts et al. believed that via increasing the temperature of the film from −196 °C to −183 °C, sufficient energy has been provided to allow relatively facile entry of oxygen into the subsurface region [10]. Heating above 327 °C for Ni films leads to the diffusion of oxygen atoms into the bulk and the partial reduction of the surface Ni to its metallic state [11]. Grain size can also serve as a significant factor to affect the oxidation behavior of metal materials because the surface energy of the film with small grains is higher than that of big grain film. Above all, eliminating or reducing the possibility of erbium to be oxidized is an effective way to promote its capability as T storage material. However, the mechanism of oxidation behavior of erbium film and the factors influencing the oxidation behavior at lower substrate temperatures are not clear up to now. In this study, erbium films are deposited on the rolled molybdenum substrates with substrate temperatures

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ranging from 200 °C to 650 °C, in order to understand the effect of substrate temperature on the oxidation behavior.

2. Experimental procedure

A series of 2–4 μm erbium thick films were electron-beam evaporated on the rolled molybdenum (Mo) substrates and mechanically polished-molybdenum (PMo, surface roughness RMS < 5 nm) substrates at substrate temperatures of 200 °C–650 °C. Evaporation rates detected by IC5 thin film deposition controller (Inficon, USA) were 5 or 10 nm/s. Before deposition, all substrates were ultrasonically cleaned with ethanol and subsequently in acetone. In addition, the molybdenum holder and molybdenum substrates were outgassed by increasing the temperature from room temperature to 700 °C and heating for 2 h at 700 °C. The source material erbium bulk (99.95% purity, 25 mm in diameter) were outgassed by melting it using electron-beam to remove the surface oxide layer and possible residual gases absorbed from air. After outgas of substrates and source material, the molybdenum substrates were cooled to the desired temperature for film deposition and the vacuum pressure was better than 3.0×10^{-6} Torr. The erbium was then deposited onto the substrates with the direction parallel to the substrate normal. To obtain uniform film, the sample holder was rotated during deposition and the distance between source material and sample holder was ~20 cm.

The microstructure of the as-deposited erbium thick films were identified by XRD using a X'pert PRO MPD (Panalytical, Holand) with a Cu Kα radiation. The cross-section morphologies of films were characterized using a Apollo 300 FE-SEM (Obducat CamScan, UK). The XPS ion sputtering depth profiling of oxygen and erbium was performed for three representative erbium films with different surface colors by using a ESCALAB 250Xi spectrometer (Thermo Scientific, UK). The X-ray source was a non-monochromatic Al Kα (150 W) lamp at photon energy 1486.6 eV. The residual gas pressure in the analyzing chamber was typically less than 1.8×10^{-9} mbar. The specimens were ion sputtered using an argon gun operated at 3 keV to conduct in-depth profile analysis and to determine the thickness of the oxide layer. The argon ion beam with current of 2.1 μA was rastered over a 0.6 mm × 0.6 mm area yielding a sputtering rate of ~25 nm/min and the etching thickness was measured by Dektak 150 Stylus Profiler (Veeco, USA).

3. Results and discussion

The erbium films were deposited onto Mo and PMo substrate at different substrate temperatures of 200 °C, 350 °C, 450 °C, 550 °C, and 650 °C. For all samples, the color of as-deposited erbium films changes from black to gray with the increasing substrate temperature. The most clear color change occurs between 350 and 450 °C. Therefore, only three representative samples (listed in Table 1) with different colors deposited at substrate temperature of 350 and 550 °C were characterized by the XPS depth profiling technique. There is no diffraction peak of erbium oxide in the XRD patterns of PMo-350, Mo-550 and PMo550 samples (as shown in Fig. 1), which

Table 1
Sample specifications.

Substrate	Substrate temperature (°C)	Surface color	Thickness of oxide layer (nm)	Designation
PMo	350	Black	~75	PMo-350
Mo	550	gray	~50	Mo-550
PMo	550	gray	~50	PMo-550

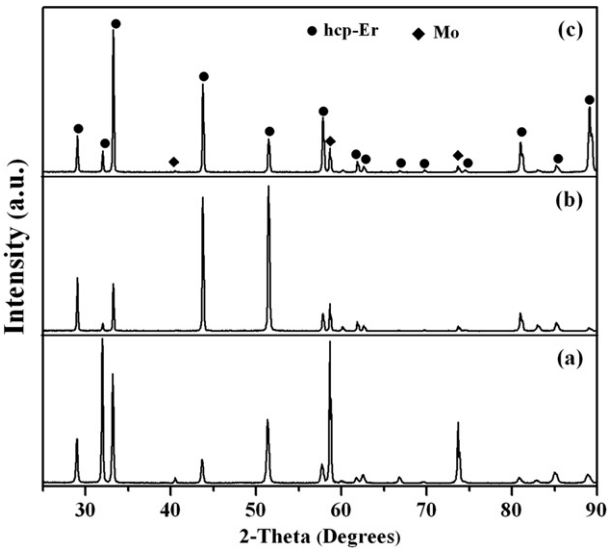

Fig. 1. The XRD patterns of erbium thick films deposited on (a) PMo substrate at substrate temperatures of 350 °C and (b) Mo, (c) PMo substrate at 550 °C. The structures of hexagonal-close-packed (hcp) and body-centered-cubic (bcc) for erbium (Er) and molybdenum (Mo) are observed in each of the XRD patterns, whereas the diffraction peak of erbium oxide does not appear for any sample.

indicates that the oxide layer is extremely thin in comparison to the thickness of erbium film.

Evolution of the Er 4*d* and O 1*s* core level spectra as a function of etching time are shown in Fig. 2 for PMo-350, Mo-550 and PMo-550 samples. From the Er 4*d* spectra in Fig. 2(a), (c) and (e), it can be seen that only one broad peak appears at binding energy (BE) of ~169.25 eV in the as-deposited erbium films, which is similar to pure Er_2O_3 in shape and peak position. However, a doublet appears in the Er 4*d* region (BE ≈ 167.15 and 169.25 eV) just after argon ion sputtering for 30 s, which indicates that the oxide layer has been removed and the metallic erbium is exposed [12]. The O 1*s* spectra show two peaks (Fig. 2(b), (d) and (f)) in the as-deposited films. One peak at 531.30 eV is corresponding to metal oxide and the other at 533.05 eV is corresponding to the hydroxide [13] which disappears after argon etching for 30 s. The presence of these two peaks indicates that Er_2O_3 as well as $Er(OH)_3$ are found in the sample surface. Tewell et al. also suggested that the lower energy peak in the O 1*s* region is attributed to Er_2O_3 and the higher one is attributed to oxygen from carbonates or alcohols [12]. The intensity of O 1*s* signal will decrease to zero after etching for 1800 s, 120 s and 240 s for the PMo-350, Mo-550 and PMo-550 samples, respectively.

The relative concentration of oxygen/erbium (O/Er) with respect to etching time is displayed in Fig. 3. The relative concentration of erbium and oxygen is equal to the integration area divided by the sensitivity factor. The integration area is obtained by subtracting the shirley background from the original XPS data between 160-205 eV and 528–536 eV for Er 4*d* and O 1*s*, and the sensitivity factors are 2.0 and 0.67 for the Er 4*d* and O 1*s* lines [14]. Fig. 3 shows that the O/Er decreases to zero after 240 s argon etching for PMo-350 and 180 s for Mo-550 and PMo-550. The thickness of oxide layer of film deposited at 350 °C is thicker than that deposited at 550 °C, which is consistent with the surface color change of samples, *i.e.* the black color suggests that the thicker oxide layer formed during deposition. The argon sputtered spots show the silvery white color of erbium and the thickness of oxide layer were measured immediately by a stylus profiler. In addition, XPS results can also be used to calculate the thickness of oxide layer based on the etching rate (~25 nm/min). The thickness of oxide layer is 75 nm for PMo-350 and 50 nm for Mo-550 and PMo-550,