Fabrication processing effects on the microstructure and morphology of erbium film*

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(Received 29 September 2011; revised manuscript received 26 February 2012)

The effect of substrate temperature on the microstructure and the morphology of erbium film are systematically investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). All the erbium films are grown by electron-beam vapor deposition (EBVD). A novel preparation method for observing the cross-section morphology of the erbium film is developed. The films deposited at 200 °C have (002) preferred orientation, and the films deposited at 450 °C have a mixed (100) and (101) texture, due to the different growth mechanisms of surface energy minimization and recrystallization, respectively. The peak positions and the full widths at half maximum (FWHMs) of erbium diffraction lines (100), (002), and (101) shift towards higher angles and decrease with the increasing substrate temperature in a largely uniform manner, respectively. Also, the lattice constants decrease with increasing temperature. The transition in the film stresses can be used to interpret the changes in peak positions, FWHMs, and lattice constants. The stress is compressive for the as-growth films, and is counteracted by the tensile stress formed during the process of temperature cooling to room temperature. The tensile stress mainly originates from the difference in the coefficients of thermal expansion of the substrate–film couple.

Keywords: erbium film, substrate temperature, preferred orientation, columnar grain

PACS: 61.05.–a, 81.10.Jt, 81.10.–h, 81.15.Jj **DOI:** 10.1088/1674-1056/21/7/076101

1. Introduction

Erbium (Er) has been extensively studied both theoretically[1] and experimentally[2−7] in recent years. One of the most important applications of erbium in the nuclear industry is that a film with a thickness of 3–6 μm can be used as the tritium (T) target material, which is the key component of a neutron generator.[8−10] The major advantage of erbium for the potential application is that the erbium dihydride film has high thermal stability[11−13] in comparison to Ti,[10,13] i.e., the chemisorbed hydrogen isotopes[14] in erbium hydrides would be decomposed at a higher temperature in comparison to that of Ti. And helium (He), generated by the decay of T with a half-life of 12.32 years,[3,7] would be released from the Er–T–He ternary system at a critical rate when the ratio of generated He to Er reaches 0.32.[7,15,16]

The growth mechanism of erbium film has been investigated by many researchers,[4,17,18] and the results demonstrate that the microstructures and morphologies of erbium films are sensitive to the deposition parameters, including the substrate temperature,[4,17,18] the deposition rate,[4,17,18] the substrate material,[4,17] the residual gases,[4,17−19] and the surface contamination.[18] The preferred orientation of erbium film changes with the above deposition condition.[4,20] It was also found that the grain size increases with the increase of the substrate temperature and the deposition rate, and this dependence on the substrate temperature is consistent with the activation energy model proposed by Grovenor *et al.*[21] The thermodynamic property for absorbing T, a core

*Project supported by the National Natural Science Foundation of China (Grant No. 10976007), the Fundamental Research Funds for the Central Universities, China (Grant No. ZYGX2009J040), the Science and Technology Foundation of CAEP, China (Grant No. 2009A0301015), and the Major Program of the National Natural Science Foundation of China (Grant No. 91126001).

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parameter for estimating its application value in nuclear technology,[22] is significantly affected by the microstructure of the erbium film. Parish *et al.*[20] found that ErD_2 grain sizes are strongly influenced by the prior metal grain size, with small metal grains leading to large ErD_2 grains. One can expect that the critical release of He[15,16] from $ErT_{2-x}He_x$ would be easily conducted by the microstructure of the erbium film. Therefore, it is very important to understand the dependence of the morphology and microstructure of the erbium film on the deposition conditions, which can improve the properties of erbium film for absorbing T and stacking He. Generally, the grain size and the intrinsic stress of the film would be changed by the heat annealing treatment.[23,24] The vacuum annealed In_2O_3 thin films display a grain size enlargement and a preferential orientation.[24]

Although the growth mechanism of erbium film has been previously reported by Gu *et al.*[4] and Savaloni *et al.*,[17,18] the preferred orientations of erbium thick films, the peak positions of erbium diffraction lines, and the full widths at half maximum (FWHMs) changing with the substrate temperature are not included. In this work, the effects of the substrate temperature on the morphology and the microstructure of the erbium film are systematically explored.

2. Experiment

Two series of erbium thick films were electron-beam evaporated onto rolled molybdenum (Mo) at substrate temperatures ranging from 200 °C to 650 °C, and the deposition rate was either ∼0.5 nm/s or ∼10 nm/s. The evaporation rate was detected by an IC5 thin film deposition controller (Inficon, USA). Before the deposition, all the substrates were ultrasonically cleaned with ethanol and subsequently in acetone. In addition, the molybdenum holder and the 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), was outgassed by melting it using an electron beam to remove the surface oxide layer and the residual gases absorbed from air. After the outgas of the substrates and the source material, the molybdenum substrates were cooled to the desired temperatures for film growth. Once the vacuum pressure was lower than 4.0×10^{-4} Pa, the erbium was deposited on the substrates in a direction parallel to the substrate normal direction. To obtain a uniform film, the substrate holder was rotated during the deposition, and the distance between the source material and the substrate holder was ∼20 cm.

The microstructures of the erbium films were preliminarily identified by XRD using an X'pert PRO MPD (Panalytical, Holland) with the Cu $K\alpha$ radiation. Each pattern was registered from 15° to 90° with a step of 0.04° in 2θ and 1 s in count time. The surface and the cross-section morphologies of the as-growth films were obtained using an Apollo 300 field emission scanning electron microscope (FE-SEM, Obducat CamScan, UK).

The schematic diagram for simply observing the cross-section morphology of the erbium film is plotted in Fig. 1. Firstly, a gap in the middle of the line along the diameter was mechanically cut after the molybdenum substrate was rolled into a wafer, followed by ultrasonically cleaning with ethanol and subsequently in acetone. Secondly, the erbium was deposited onto the above substrate. The erbium film could be found on the surface of the substrate and in the gap, but with the exception of the area in the fringe of the gap. Finally, the substrate was fractured into two pieces, and the cross-section morphology of the film could be easily observed in the fringe area of the gap. Although the cross-section morphology of the film was not flat, as the molybdenum substrate was not mechanically polished, the kind of grain and the tendency of grain size of the erbium film changing with the substrate temperature were clearly identified using the presented technique (shown in Fig. 1). However, the thickness of film could not be evaluated accurately using the observed cross-section morphology, especially when the substrate temperature exceeded 450 °C.

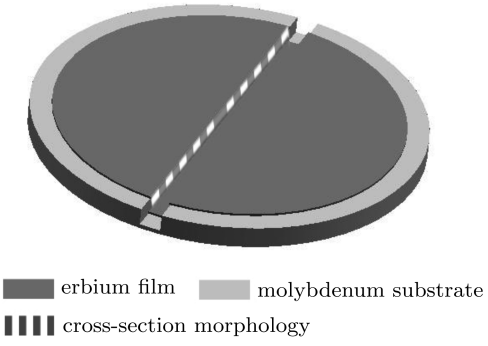


Fig. 1. Schematic diagram for observing the cross-section morphology of erbium film.

3. Results and discussion

The fabrication parameters used to grow the erbium films are summarized in Table 1, including the substrate temperatures and the deposition rates. The nomenclatures of the films are provided based on the corresponding deposition conditions (right column in Table 1). The approximate thicknesses of the erbium films are equal to the masses divided by the product of the density of erbium (9.05 g/cm^3) and the surface area of film. As can be seen, the films deposited at a higher rate (∼10 nm/s) are much thicker than that deposited at ∼0.5 nm/s. The deposition rate cannot be accurately controlled when the rate is relatively high. Based on our experimental results (not shown here), the microstructure and the morphology of the film would not be apparently affected by the film thickness when the thickness of the film is at the order of μm.

Table 1. Fabrication parameters for erbium film deposition.

Deposition rate/nm·s^{-1}	Substrate temperature/°C	Thickness of film/μm	Designation
∼ 0.5	200	∼ 1.73	Er200-0.5
	350	∼ 1.26	Er350-0.5
	450	∼ 1.37	Er450-0.5
	550	∼ 1.32	Er550-0.5
	650	∼ 1.74	Er650-0.5
∼ 10	200	∼ 5.91	Er200-10
	350	∼ 5.88	Er350-10
	450	∼ 3.76	Er450-10
	550	∼ 7.25	Er550-10
	650	∼ 6.21	Er650-10

The surface and the cross-section morphologies (in the inset) of all the specimens are shown in Fig. 2. The columnar grains[17−21] are observed for all specimens in the cross-section morphologies, which is consistent with the structure-zone models (SZMs) proposed by Savaloni *et al.*[17,18] and Gu *et al.*[4] for the specific case of erbium thin films. The SZMs illustrate that the structure of polycrystalline thin film is determined by the processing parameters, primarily the homologous substrate during deposition defined as T_s/T_m, where T_s is the substrate temperature in Kelvin, and T_m is the melting point of the film material in Kelvin. Here, the value of T_s/T_m ranges from 0.26 to 0.51 for the corresponding substrate temperatures increasing from 200 °C to 650 °C, which is in accordance with the structure characteristics (columnar grains) of zone T ($0.2 < T_s/T_m < 0.3$), zone 2 ($0.3 < T_s/T_m < 0.5$), and zone 3 ($T_s/T_m > 0.5$) resulted from the SZMs.[4] The zone T structure is columnar, consisting of tapered units defined by voided growth boundaries of the type. The zone 2 structure consists of columnar grains, which are defined by metallurgical grain boundaries and an increase in width with an increase of T_s/T_m in accordance with activation energies typical of the surface diffusion. The zone 3 structure has shown to be consisted of squat uniform columnar grains, the diameter of which exceeds the thickness.[4]

As can be observed from Fig. 2, the grain sizes (widths of columns) of erbium films increase with the increasing substrate temperature whatever the deposition rate is. At 200 °C, the separated grains are observed, and pores exist between the grains. The surface is smoothened by the improvement of surface diffusion of erbium ad-atoms when the substrate temperature reaches 350 °C. Indeed, it is difficult to distinguish different grains from the surface morphology at the substrate temperature of 650 °C. The variation of deposition rate (0.5 nm/s and 10 nm/s) does not influence this development significantly. The above phenomena may be attributed to the different diffusion mechanisms of erbium ad-atoms, which are surface diffusion, bulk diffusion, and recrystallization for zone T, zone 2, and zone 3, respectively.[21] The dependence of grain dimensions on T_s has been used in an attempt to characterize the rate controlling process in the grain development of the films, i.e. at any given temperature, boundaries will migrate at different rates, and the lower the temperature, the smaller the proportion of mobile boundaries. Therefore, only a small minority of the grains are expected to grow at a low substrate temperature (200 °C), while almost all boundaries are mobile at the temperature exceeding 350 °C.[21]

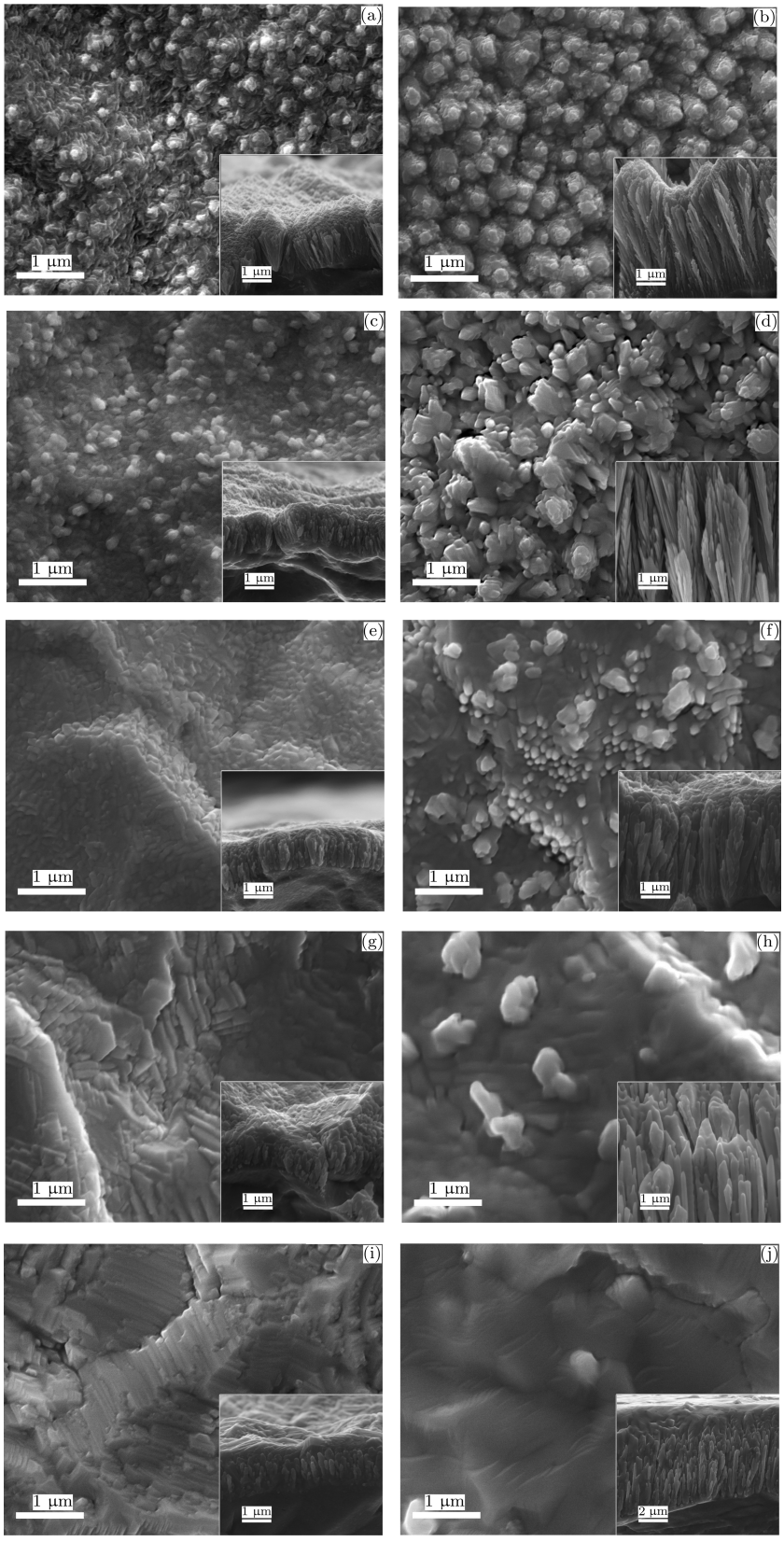


Fig. 2. Surface and cross-section (in the inset) morphologies of erbium films, which are deposited at the substrate temperatures of (a) 200 °C, (b) 200 °C, (c) 350 °C, (d) 350 °C, (e) 450 °C (f) 450 °C, (g) 550 °C, (h) 550 °C, (i) 650 °C and (j) 650 °C, with deposition rates of either 0.5 nm/s (left row) or 10 nm/s (right row).

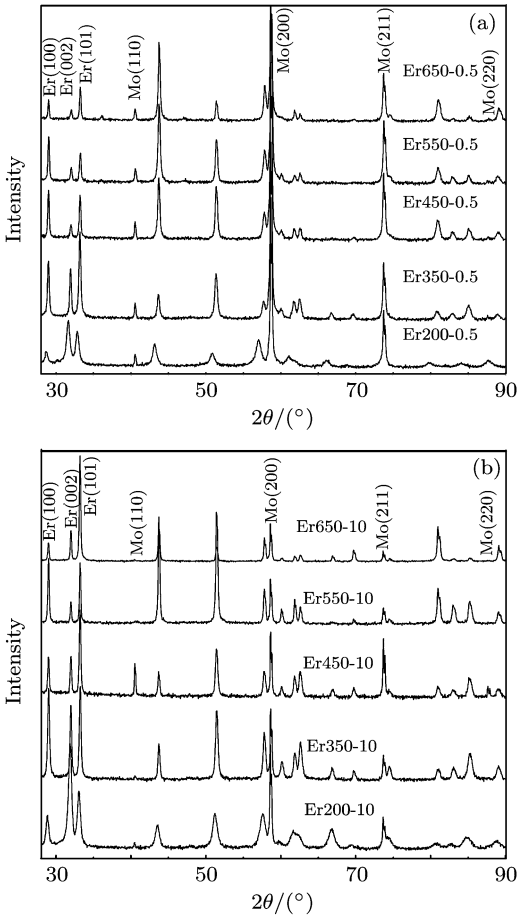


Fig. 3. The XRD patterns of as-growth erbium films, which are deposited at sbstrate temperatures ranging from 200 °C to 650 °C, with deposition rates of (a) 0.5 nm/s and (b) 10 nm/s.

Figure 3 shows the XRD patterns of the erbium films deposited at different substrate temperatures with deposition rates of 0.5 nm/s (Fig. 3(a)) and 10 nm/s (Fig. 3(b)). The erbium films deposited at 200 °C have (002) preferred orientation, and the films deposited at higher temperatures (350 °C to 450 °C) have mixed (100) and (101) textures. From Fig. 3, it is evident that all the molybdenum substrates have (200) preferred orientation in contrast to the calculated XRD data (PDF card 00-004-0809), which is independent of the substrate temperatures. It is clear that the relationship between the preferred orientations of molybdenum and erbium is insignificant. The regulation of the preferred orientation of the erbium film changing with the substrate temperature is contrary to the result obtained by Parish *et al.*[20] The (002) texture of the erbium film deposited at 200 °C should be conducted by the theory of surface energy minimization, which shows that the basal plane (001) has the minimum surface energy for the hexagonal-close-packed (hcp) metal.[25] So from the surface energy minimization theory, the (001) texture should be favored in the hcp films, which is consistent with the experimental results.[26] However, the mixed (100) and (101) texture may be dominated due to the diffusion of ad-atoms and the recrystallization of film grains.[27]

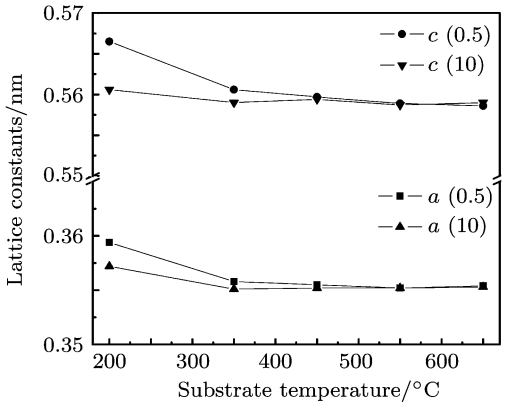


Fig. 4. Lattice constants of erbium films as a function of substrate temperature (200 °C to 650 °C) and deposition rate (0.5 nm/s or 10 nm/s).

The peak positions (2θ) of erbium diffraction lines (100), (002), and (101) change with the substrate temperatures, as depicted in Fig. 3. For all selected erbium diffraction lines (100), (002), and (101), the peak positions shift towards higher angles with the substrate temperature increasing from 200 °C to 350 °C, and remain constant when the temperature is higher than 350 °C. This conclusion is still unaffected by the deposition rates. The lattice constants calculated from the XRD data are shown in Fig. 4. The lattice constants of erbium, a and c, decrease obviously with the substrate temperature increasing from 200 °C to 350 °C and reach steady values after 350 °C. The FWHMs of erbium diffraction lines (100), (002), and (101) changing with the substrate temperatures are listed in Table 2. Generally, it is clear that the FWHMs of the selected diffraction lines decrease with the increasing substrate temperature in a largely uniformly manner, although slight discrepancies can be observed for (002) and (101) diffraction lines. As for (002) diffraction lines, the FWHMs first decrease with the substrate temperature increasing to 350 °C, and then slightly increase with the substrate temperature up to 450 °C, followed by a continuous decrease tendency with the substrate temperature. The increase in FWHM from 350 °C to 450 °C might be related to the relative intensity variation of the erbium diffrac-

tion lines with the substrate temperature. The decrease in FWHM originates from the increase in grain size and the relaxation of intrinsic stress. Although it is difficult to quantify the dominating factor here, the increase of grain size and the relaxation of stress with high temperature annealing were reported by many researchers.[23,24,28] Based on all the XRD patterns plotted in Fig. 3, the diffraction lines of Mo substrates are always unchanged whatever the fabrication parameters are.

Table 2. The FWHMs of diffraction lines (100), (002), and (101) of erbium films deposited at 0.5 nm/s and 10 nm/s as a function of substrate temperature (200 °C to 650 °C), the errors are displayed in the parentheses.

Deposition rate /nm·s^{-1}	Substrate temperature/°C	FWHM of erbium diffraction lines in 2θ/(°)		
		(100)	(002)	(101)
∼ 0.5	200	0.332 (0.031)	0.364 (0.008)	0.378 (0.010)
	350	0.157 (0.004)	0.152 (0.005)	0.167 (0.003)
	450	0.127 (0.004)	0.189 (0.020)	0.130 (0.004)
	550	0.121 (0.004)	0.179 (0.020)	0.161 (0.006)
	650	0.100 (0.007)	0.174 (0.020)	0.127 (0.004)
∼ 10	200	0.275 (0.024)	0.328 (0.006)	0.346 (0.013)
	350	0.165 (0.003)	0.142 (0.004)	0.155 (0.003)
	450	0.138 (0.006)	0.153 (0.013)	0.140 (0.003)
	550	0.115 (0.003)	0.106 (0.009)	0.104 (0.003)
	650	0.112 (0.004)	0.104 (0.002)	0.104 (0.001)

All the above results, including the changes in peak positions, lattice constants, and FWHMs are attributed to the evolution of compressive and tensile stresses inside the films during the deposition processing. A compressive stress in the erbium film is not surprising, as the electron-beam vapor deposition is used for growth. The compressive stress in the erbium film is enhanced due to the energetic grain bombardment during deposition.[29] Recently, research by Chason *et al.*[30] identified grain boundaries as an important factor in generating a compressively-stressed continuous film. However, the tensile stress would be led by the difference in the coefficient of thermal expansion (CTE) of erbium (12.2×10^{-6} °C) and molybdenum (4.8×10^{-6} °C) materials,[31] i.e., the different shrinkages of erbium and molybdenum when the substrate temperature is cooled to room temperature. The transition of stress from compressive to tensile is expected during the cooling process of the film. The reason for the transition in film stress is that the compressive stress formed during the deposition is counteracted by the tensile stress improved during the cooling process. The higher the substrate temperature for the film growth is, the larger the tensile stress increment is, leading to the shrinkage of film being clearer for the higher as-growth temperature. Therefore, the films deposited at a low substrate temperature are still in compressive station, while the compressive stress is nearly counteracted by the tensile stress for the films deposited at a higher temperature. The lattice constants are larger when the film is in the compressive state. So, the transition in film stress can be used to explain the results that the peak positions of erbium diffraction lines shift towards higher angles and the lattice constants of erbium decrease with the increasing substrate temperature. The evolution of stress in ScD_2/Cr thin films fabricated by evaporation and high temperature reaction has been reviewed in detail.[32] The reaction of scandium metal with deuterium at the elevated temperature to form a stoichiometric dideuteride phase leads to a large compressive in-plane film stress, resulted from an increased atomic density compared with the as-deposited metal film. A tensile stress develops due to the mismatched CTE of the substrate-film couple.[32] Yuan *et al.*[28] demonstrated that the lattice constant decreases and is close the bulk one, which indicates that the compressive strains in the In_2O_3 films are gradually relaxed as the the annealing temperature increases. Zhou *et al.*[23] found that with the increasing annealing temperature, the compressive stress decreases due to the elimination of defects and the grain growth that causes the lateral shrinkage of film and produces a relative tensile stress.

4. Conclusion

A preparation method for observing the cross-section morphology of erbium film is described. The columnar grains are observed for all the presented erbium films, and the grain sizes increase with the increasing substrate temperature due to the coalescence and the migration of grains during the deposition. The films deposited at 200 °C have (002) preferred orientation, while the films deposited at 450 °C have mixed (100) and (101) texture. The mechanisms of surface energy minimization and recrystallization can be used to explain the different preferred orientations for films deposited at low and higher substrate temperatures. The peak positions and the FWHMs of erbium diffraction lines (100), (002), and (101) shift towards higher angles and decrease with the increasing substrate temperatures in a largely uniform manner, respectively. The lattice constants decrease with the increasing temperature. All the changes in peak positions, FWHMs, and lattice constants can be explained by the transition of the film stress. The stress is compressive for the as-growth film and is counteracted by the tensile stress formed during the process cooling down to room temperature. The tensile stress originates from the difference in the coefficient of thermal expansion of molybdenum and erbium materials.

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