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# Thermally induced evolution of optical and structural properties of Er<sub>2</sub>O<sub>3</sub> films grown on Si substrates by thermal atomic layer deposition

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## A B S T R A C T

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Crystal structure  
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Thermally induced evolution of structural and optical properties of Er<sub>2</sub>O<sub>3</sub> films prepared by atomic layer deposition was investigated. The films were grown on Si substrates by water-assisted approach from (tris(methylcyclopentadienyl)erbium(III)). As-deposited films showed cubic Er<sub>2</sub>O<sub>3</sub> phase, and compressive stress. Isochronal (30 min) heating at 600–1100 °C in nitrogen flow caused strain relaxation, decrease of the lattice parameters and the increase of coherent domain size. Besides, in the films annealed at 1000–1100 °C, the formation of Er silicate phase was observed. This phase formed due to Si diffusion from substrate in film volume, and the presence of Si was found not only at the film/substrate interface, but also on the top surface of the film. This fact was explained by spinodal decomposition of Er silicate with the formation of Er<sub>2</sub>SiO<sub>5</sub> phase on top surface. It was shown that both oxygen vacancies and Er<sup>3+</sup> ions contribute to light emission, however, no energy transfer from vacancies to Er<sup>3+</sup> ions was detected.

## 1. Introduction

Nowadays, more and more attention is paid to erbium oxide films owing to their applications in microelectronics [1,2], photonics [3], as well as protective and anticorrosion coatings [4]. Physical and chemical vapor deposition [3,5,6], sol-gel method [7], magnetron sputtering [8] are used for film growth. In recent years, atomic layer deposition (ALD) becomes more attractive. However, only a few groups reported on the successful fabrication of Er<sub>2</sub>O<sub>3</sub> films [2,9,10,11]. In this work, we report on the effect of high-temperature annealing on optical and structural properties of Er<sub>2</sub>O<sub>3</sub> films grown by water-assisted ALD approach.

## 2. Experimental details

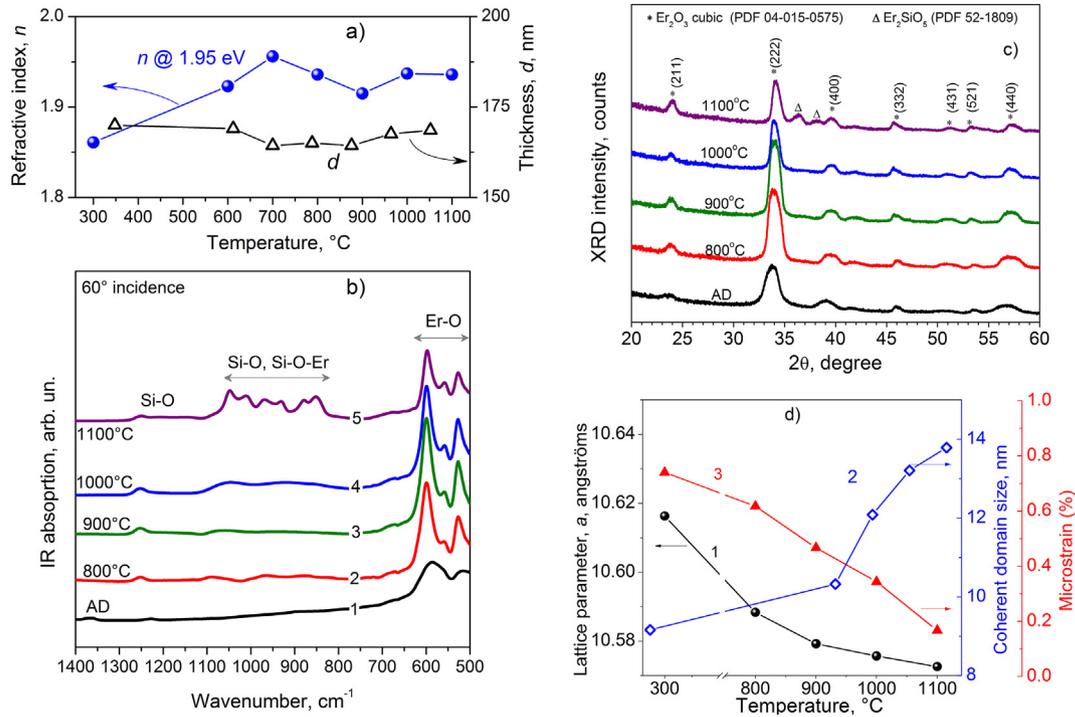
Er<sub>2</sub>O<sub>3</sub> films were grown on p-type Si substrates in a Picosun<sup>®</sup> 200 Advanced ALD tool using (tris(methylcyclopentadienyl)erbium(III)) (Er(CpMe)<sub>3</sub>, CAS No. 39740–10-5) as precursor and water as oxidant. During deposition, the substrate was kept at 300 °C

and Er(CpMe)<sub>3</sub> was heated at 170 °C. The Er(CpMe)<sub>3</sub>/H<sub>2</sub>O pulse/purge time sequence was 1.6 s/2.0 s/0.1 s/2.0 s. The film thickness was about 170 nm. After deposition, the substrates were cut into samples that were submitted to isochronal (30 min) annealing at T<sub>A</sub> ranging from 500 to 1100 °C in nitrogen flow. The samples were studied at room temperature by means of Spectroscopic Ellipsometry, Fourier Transform Infrared (FTIR) spectroscopy, Photoluminescence (PL), X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM) and Energy-Dispersive X-Ray spectroscopy (EDX) methods. More details about experimental methods are given in the supplement section.

## 3. Experimental results and discussion

### 3.1. Evolution of refractive index and film thickness with T<sub>A</sub>

As-deposited films demonstrated the refractive index  $n = 1.85$ – $1.861$  (at 1.95 eV) similar to that reported for Er<sub>2</sub>O<sub>3</sub> in Refs. [12,13]. Thermal treatment results in its non-monotonic variation (Fig. 1,a, Fig. 1S). The T<sub>A</sub> increase up to 700 °C causes the  $n$  rising up to 1.952–1.956 (at 1.95 eV) along with some thickness decrease, which testifies to the film crystallization and densification. Further T<sub>A</sub> rising causes the  $n$  decrease down to 1.935–1.937 (Fig. 1,a) due to the formation of the phase with lower refractive index, for



**Fig. 1.** Effect of annealing temperature on: a) refractive index and thickness of the films; b) FTIR spectra (recorded with 60° incidences of excitation light); c) grazing-incidence XRD patterns ( $\omega = 0.5^\circ$ ;  $\text{Co } K_{\alpha, \lambda} = 1.78897 \text{ \AA}$ ); d) lattice parameter (1), coherent domain size (2) and microstrain (3). The curves in b) and c) are shifted vertically for clarity. The data at  $T_A = 300^\circ \text{C}$  in d) correspond to as-deposited film.

instance, some pores or cavities or  $\text{SiO}_x$  and Er silicate phases. The analysis of absorption spectra (Fig. 1S,d), using general Tauc model and assuming  $\text{Er}_2\text{O}_3$  films as allowed transitions indirect bandgap material similar to Ref. [13], showed that the annealing results in some decrease of bandgap value from  $E_g = 5.28 \text{ eV}$  (as-deposited films) down to  $E_g = 4.95 \text{ eV}$  ( $T_A = 1100^\circ \text{C}$ ) (Fig. 1S,d). This  $E_g$  behavior is the evidence of the formation of Er silicate phase in the films.

### 3.2. Evolution of FTIR spectra and XRD patterns with $T_A$

The FTIR spectra of as-deposited films showed Er-O vibration band in the  $400\text{--}650 \text{ cm}^{-1}$  range (Fig. 1,b) and OH-vibration band in the  $3200\text{--}3600 \text{ cm}^{-1}$  range (not shown here). This band is due to the presence of residual OH groups in the film after deposition. An annealing at  $T_A = 500\text{--}600^\circ \text{C}$  caused desorption of OH groups only. For  $T_A = 700\text{--}1100^\circ \text{C}$ , instead of broad Er-O band some resolved peaks appear, being sharper for higher  $T_A$  (Fig. 1,b). Besides, additional Si-O bands at  $1250$ ,  $1080$  and  $820 \text{ cm}^{-1}$  along with the Si-O-Er vibration bands were observed (Fig. 1,b) that can be explained by Si diffusion in the film volume.

Grazing-incidence XRD data supports these findings (Fig. 1,c). As-deposited films grown at  $300^\circ \text{C}$  were already crystallized in the cubic  $\text{Er}_2\text{O}_3$  phase (PDF No. 04-015-0575). The most intense peaks in the  $2\theta = 20\text{--}60^\circ$  range were found at  $2\theta = 23.48^\circ$  (2 1 1),  $33.73^\circ$  (2 2 2),  $39.10^\circ$  (4 0 0) and  $56.82^\circ$  (4 4 0) (Fig. 1,c), being shifted to lower angles in comparison with standard values. This shift is caused by mismatching in lattice parameters of the film and substrate. Indeed, for standard  $\text{Er}_2\text{O}_3$ , the  $a_{\text{Er}_2\text{O}_3} = 1.054 \text{ nm}$  value is close to twice the unit cell of Si substrate ( $2a_{\text{Si}} = 1.086 \text{ nm}$ ). However, small negative mismatch for the  $\text{Er}_2\text{O}_3$  generated its stress. For as-deposited films, it was found that  $a_{\text{Er}_2\text{O}_3} = 1.0617 \text{ nm}$  and the microstrains are  $\sim 0.74\%$  (Fig. 1,d).

A supplementary annealing leads to further film crystallization and strain relaxation. Indeed, the  $T_A$  increase up to  $1000^\circ \text{C}$  gives rise to some narrowing of XRD peaks and the gradual shift towards

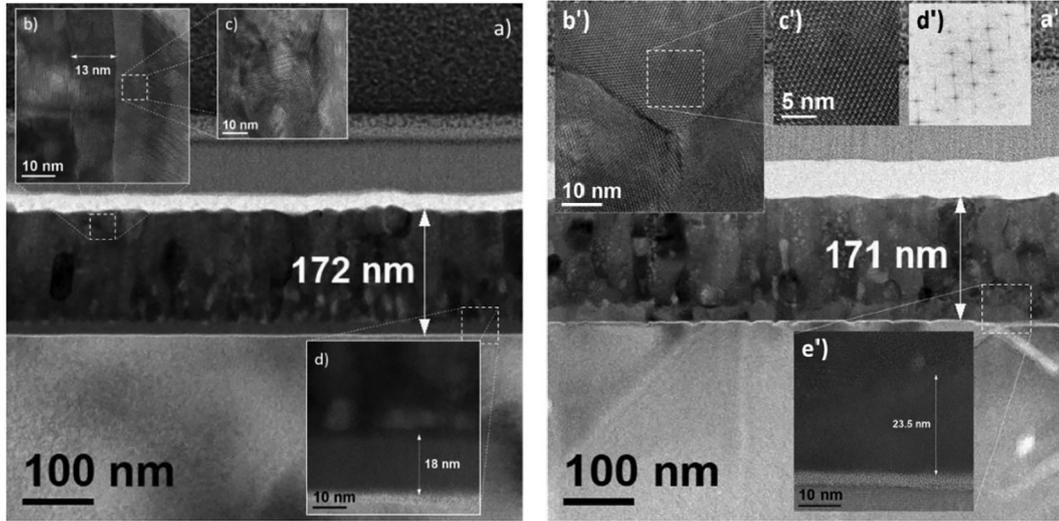
higher angles, i.e.  $2\theta = 24.06^\circ$  (2 1 1),  $34.12^\circ$  (2 2 2),  $39.64^\circ$  (4 0 0) and  $57.36^\circ$  (4 4 0) (Fig. 1,c), approaching the values of standard cubic  $\text{Er}_2\text{O}_3$ . The highest intensity of the peak at  $2\theta = 33.73^\circ$  (2 2 2) is the evidence of the preferable orientation of the film following the [1 1 1] direction. The analysis of XRD data revealed the gradual decrease of the lattice parameters down to  $1.057 \text{ nm}$  and the increase of coherent domain size from  $\sim 9 \text{ nm}$  up to  $\sim 14 \text{ nm}$  as well as stress relaxation down to  $0.17\%$  (Fig. 1,d). No any other  $\text{Er}_2\text{O}_3$  phases were distinguished in the annealed films, whereas for  $T_A = 1100^\circ \text{C}$ , additional XRD peaks appeared at  $2\theta = 35.36^\circ$  and  $38.15^\circ$  (Fig. 1,c) that can be assigned to  $\text{Er}_2\text{SiO}_5$  phase (PDF card No. 52-1809).

### 3.3. Study of the films with microscopy methods

Analysis of the surface of the same samples confirmed the formation of some grains (Fig. 2S and 3S) and appearance of some cracks at  $T_A = 900\text{--}1100^\circ \text{C}$  supporting the statement on the stress relaxation. It should be noted that not only mismatching in lattice parameters, but also the presence of OH-groups could be the reasons of this phenomenon.

To obtain information on spatial localization of  $\text{SiO}_x$  and/or Er silicate phases in the samples annealed at  $1000$  and  $1100^\circ \text{C}$ , their cross-sectional specimens were observed using TEM method. It was confirmed that the  $\text{Er}_2\text{O}_3$  grains have cubic structure. An example is shown in Fig.2, where a grain is oriented following a [1 1 1] direction (Fig. 2). Some cavities were found in the film volume and their amount increases for higher  $T_A$ . The interfacial layers with thicknesses of  $18 \text{ nm}$  ( $T_A = 1000^\circ \text{C}$ ) and  $23.5 \text{ nm}$  ( $T_A = 1100^\circ \text{C}$ ) were observed.

The EDX analyses confirmed that this layer is Er silicate (Table 1). Si atoms are distributed over the whole film annealed at  $1100^\circ \text{C}$ . However, Si content is significant only in the interfacial layer and at the film surface. This result showed that high-temperature annealing stimulates Si diffusion from the substrate



**Fig. 2.** Bright field TEM (a, a'), high-resolution TEM images (b–d, b', c', e') and selected FFT (d') of cross-section of  $\text{Er}_2\text{O}_3$  films annealed at 1000 °C (a–d) and 1100 °C (a'–e').

**Table 1**  
Chemical composition of the films annealed at 1000 and 1100 °C (Fig. 2).

Annealing temperature	Zone of the sample	Chemical composition		
		Er, at.%	O, at.%	Si, at.%
1000 °C (Fig. 2, a–d)	Interfacial layer	22.5	60.8	16.7
	Film volume	42.8	56.5	0.4
1100 °C (Fig. 2, a'–e')	Interfacial layer	22.3	68.4	10.3
	Film volume	35.9	63.1	1.0
	Near surface region	19.4	71.0	9.6

to the film volume followed by formation of Er silicate phase. However, this phase tends to decompose followed by preferential Si segregation at the film/substrate and film/air interfaces. The formation of  $\text{Er}_2\text{SiO}_5$  phase and further crystallization of  $\text{Er}_2\text{O}_3$  grains occur.

### 3.4. PL properties of the films

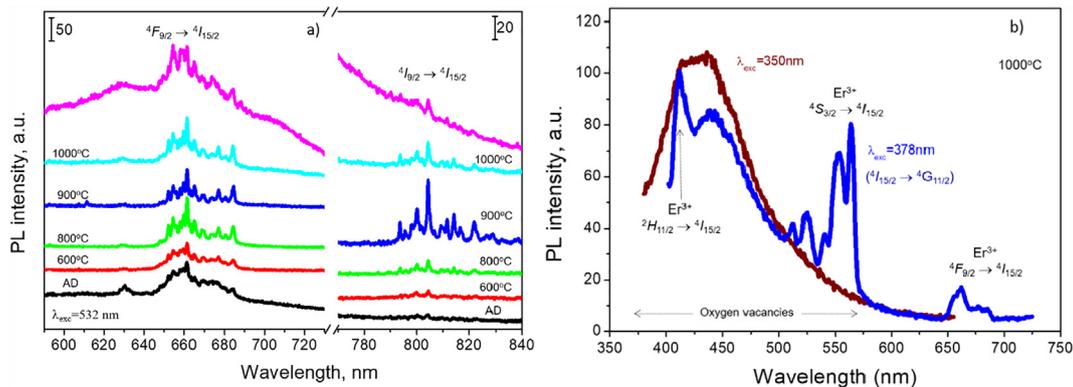
Fig. 3,a shows PL spectra recorded under “resonant” excitation (532 nm corresponding to  $\text{Er}^{3+}$  absorption in the  $^4I_{15/2} \rightarrow ^4H_{11/2}$  transition). Two main bands due to the  $^4F_{9/2} \rightarrow ^4I_{15/2}$  (650–700 nm) and  $^4I_{9/2} \rightarrow ^4I_{15/2}$  (780–830 nm) are seen. In the as-deposited films, the  $\text{Er}^{3+}$  related peaks are broad testifying some disorder in film volume. Annealed films ( $T_A = 800\text{--}900$  °C) showed sharp peaks (Fig. 3,a) that confirm the presence of Er ions in crystalline host.

Further  $T_A$  rise results in the appearance of broad PL bands peaked near 620 and 700 nm, being overlapped with  $\text{Er}^{3+}$  PL bands (Fig. 3). The comparison of the evolution of structural and PL properties allowed assuming that these broad PL components are due to Er silicate phase formation.

To investigate the potential energy transfers from host defects to  $\text{Er}^{3+}$  ions, PL spectra were recorded also under non-resonant (350 nm) and resonant (378 nm, corresponding to  $^4I_{15/2} \rightarrow ^4G_{11/2}$  absorption for  $\text{Er}^{3+}$  ions) excitation. It turned out that under excitation with 350 nm light, the PL spectrum is broad and featureless (Fig. 3b), due to carrier recombination via the host defects such as oxygen vacancies. At the same time, under 378-nm excitation, sharp peaks related to  $\text{Er}^{3+}$  PL emission appeared. Thus, both host defects such (as oxygen vacancies) and  $\text{Er}^{3+}$  ions contribute to light emission, whereas no energy transfer from oxygen vacancies to Er ions was found.

### 4. Conclusions

The effect of annealing treatment on structural and optical properties of  $\text{Er}_2\text{O}_3$  films was studied. Only cubic  $\text{Er}_2\text{O}_3$  phase was detected in as-deposited films and in those annealed at  $T_A < 900$  °C. Annealing at  $T_A = 900\text{--}1100$  °C stimulates formation of Si-rich amorphous interfacial layer, whereas at  $T_A = 1100$  °C, Er silicate phase (consistent with  $\text{Er}_2\text{SiO}_5$ ) appeared on film surface



**Fig. 3.** a) Evolution of PL spectra of  $\text{Er}_2\text{O}_3$  films with  $T_A$ . Excitation light wavelength is 532 nm. The spectra are shifted in vertical direction for clarity. b) PL spectra of the film annealed at 1000 °C recorded under non-resonant (350 nm) and resonant (378 nm) excitations.

due to Si diffusion from substrate. Both host defects (like oxygen vacancies) and  $\text{Er}^{3+}$  ions brought contributions to PL emission.

### CRediT authorship contribution statement

**L. Khomenkova:** Conceptualization, Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing. **M.-P. Chauvat:** Data curation, Investigation, Visualization, Writing - review & editing. **P. Marie:** Data curation, Formal analysis, Visualization, Writing - review & editing. **C. Frilay:** Resources, Writing - review & editing. **F. Lemarié:** Resources, Writing - review & editing. **S. Boudin:** Resources, Writing - review & editing. **X. Portier:** Data curation, Investigation, Visualization, Validation, Writing - review & editing. **N. Ratel-Ramond:** Data curation, Investigation, Visualization, Validation, Writing - review & editing. **C. Labbé:** Investigation, Validation, Writing - review & editing. **J. Cardin:** Investigation, Formal analysis, Visualization, Validation, Writing - review & editing. **F. Gourbilleau:** Supervision, Project administration, Validation, Writing - review & editing.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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