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# Photolithographic patterning of nanocrystalline europium-titanate $Eu_2Ti_2O_7$ thin films on silicon substrates

Jan Mrázek [a,*], Jan Boháček [a], Soňa Vytykáčová [a], Jiří Buršík [b], Viktor Puchý [c], Džunda Robert [c], Ivan Kašík [a]

[a] Institute of Photonics and Electronics AS CR, v.v.i., Chaberská 57, 18251 Prague 8, Czech Republic
[b] Institute of Physics of Materials AS CR, v.v.i., Žižkova 22, 616 62 Brno, Czech Republic
[c] Institute of Materials SAS, Watsonova 47, 04353 Kosice, Slovakia

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ABSTRACT

Patterned highly transparent nanocrystalline europium-titanate $Eu_2Ti_2O_7$ thin films with tailored structural properties were prepared by a sol-gel approach combined with a photolithography. The amorphous thin films on silicon substrates were prepared by the sol-gel approach. Patterns were written by a photolithography process followed by wet-etching and the samples were thermally annealed forming the pure nanocrystalline phase of $Eu_2Ti_2O_7$. Written patterns were crack-free and longitudinally homogenous and their lateral dimensions remained unchanged during the annealing. The lowest width of written ribs was 10 μm. The film thickness was approximately 540 nm and the films consist of uniform nanocrystals of the size approximately 50 nm. The results can be used for preparation of patterned thin films that are suitable for a construction of integrated spintronic devices.



## 1. Introduction

The family of lanthanide titanium oxides; which crystallize in the face-centered cubic pyrochlore structure with the general formula $RE_2Ti_2O_7$ [1] (RE = rare earth element); occupies an exceptional position in the field of materials for spintronic devices [2,3]. Their internal crystal structure brings phenomenal magnetic properties that strongly depend on the incorporated RE [4]. For example, the presence of $Dy^{3+}$ or $Ho^{3+}$ ions in the matrix causes spin-ice behavior [5,6], the presence of $Er^{3+}$ ions brings antiferromagnetic properties [7], ferroelectric properties were observed for $La^{3+}$ ions [8], etc. The introduced compounds were prepared as powders as well as thin films [9,10]. However, their wider application requires the preparation of patterned films and integrated components [11]. A number of methods; such as surface micromachining [12], laser writing [11,13], micropatterning [13,14], etc.; have been used to prepare patterned ceramic coatings and nanoparticle-doped polymer hybrid films [15].

In this contribution we present a photolithographic processing of patterned europium-titanate $Eu_2Ti_2O_7$ thin films with tailored structural properties on silicon substrates. The results can be used for preparation of patterned thin films that are suitable for a construction of integrated spintronic devices.

## 2. Experimental section

### 2.1. Preparation of films

Thin films were prepared by a sol-gel method. The starting sol was prepared by an already published approach [16]. Five layers of sol were subsequently spin-coated onto 1 in. silicon wafers (N-type, ⟨1 0 0⟩, Sigma-Aldrich) by a rotation speed 3000 RPM. Each layer was densified in a rapid thermal annealing furnace (RTA) AccuThermo AW410 (Allwin21 corporation) at 500 °C for 60 s under an oxygen flow of 5 $l \cdot min^{-1}$ and a heating rate of 10 $°C \cdot s^{-1}$. The densified multilayered films were patterned or annealed in the RTA to final temperatures raising from 700 °C to 1200 °C for 60 s under an oxygen flow of 5 $l \cdot min^{-1}$ and a heating rate of 10 $°C \cdot s^{-1}$.

### 2.2. Photolithography

G-line negative photoresist FujiFilm SC900 was spin-coated on the densified multilayered film by a rotation speed 3000 RPM. The formed photoresist layer of the thickness 20 μm was dried in a drying oven at 90 °C for 20 min. The samples were arranged into a Karl Suss MA6 mask aligner and irradiated through a patterned mask by a mercury lamp. The exposition was performed for 10 s at 20 $mW \cdot cm^2$ peak intensity. The development by a spray developer Fujifilm WNRD and a drying in a drying oven at 150 °C for

* Corresponding author.
*E-mail address:* mrazek@ufe.cz (J. Mrázek).

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20 min followed the exposition. The quality of the patterned photoresist was checked by a 3D laser scanning confocal microscope Keyence. Than the samples were subsequently exposed to the mixture of hydrofluoric (Sigma-Aldrich) and nitric acid (Sigma-Aldrich) for 120 s, demi water for 300 s, and ethyl alcohol (>98%, Sigma-Aldrich) for 60 s in order to etch out the pattern in the densified multilayer. The patterned films were annealed in the RTA to 1000 °C for 60 s under an oxygen flow of 5 $l \cdot min^{-1}$ and a heating rate of 10 $°C \cdot s^{-1}$.

### 2.3. Characterization techniques

X-ray diffraction (XRD) analyses were performed on a Bruker D8 Discover diffractometer with a Bragg-Brentano geometry operating with Cu-Kα radiation (λ = 1.54056 Å, operating voltage 40 kV, current 40 mA, integration time 200 ms). The crystallized phase was compared to JCPDS data file number 23-1072 of $Eu_2Ti_2O_7$. The mean nanocrystal size was calculated using in-build operating software using a Scherrer's equation.

Scanning electron microscope (SEM) images were taken with a TESCAN Lyra 3 XMU FEG/SEM device (operating voltage 15 kV). A thin carbon layer was sputtered on the samples prior to analyses to prevent charging.

The thickness and the surface profiles of the samples were measured on an optical profilometer NewView 7300 (Zygo). The surface morphology of the thin films was analyzed by atomic force microscopy (AFM) in the contact mode using a Dimension 3100 AFM (Digital Instruments/Veeco) operated in air. We used commercial $Si_3N_4$ cantilevers with an elastic modulus of 0.56 $N \cdot m^{-1}$.

## 3. Results and discussion

### 3.1. Structural characterizations of thin films

The thermal evolution of nanocrystalline $Eu_2Ti_2O_7$ was followed by the XRD analyses. The results are demonstrated in Fig. 1. The films were fully amorphous up to 800 °C. The first diffraction pattern typical for $Eu_2Ti_2O_7$ pyrochlore structure was recorded for the sample annealed at 800 °C. The diffraction peaks were more pronounced with increasing annealing temperature. The absence of the peaks corresponding to side-formed $TiO_2$ or $Eu_2O_3$ confirmed the high purity of the nanocrystals.

The annealing temperature strongly affected the mean nanocrystal size and the final film thickness as can be seen in Fig. 2. The nanocrystal size regularly grew with annealing temperature ranging from 30 nm up to 100 nm except the sample annealed at 900 °C which showed a significant deviation from this trend. The thickness of the densified films reached almost 900 nm. Once the crystallization had occurred at 800 °C the film thickness dropped sharply below 600 nm. Further annealing above 900 °C caused a fully densification of the films resulting to the stabilization of the film thickness approximately at 535 nm. Observed nanocrystal growth and the related densification of the films show the same course as the crystallization process of $Eu_2Ti_2O_7$ powders that terminates between 900 °C and 1000 °C [17]. Annealing temperature of 1000 °C is the lowest known temperature at which the nucleation process is terminated and only the recrystallization occurs [17] and it should be considered as the optimal processing temperature.

### 3.2. Microstructure of patterned films

SEM images of the patterned films are shown in the Fig. 3. The bright and dark regions correspond to the $Eu_2Ti_2O_7$ nanocrystals and the silicon substrate, respectively. Presented method allowed

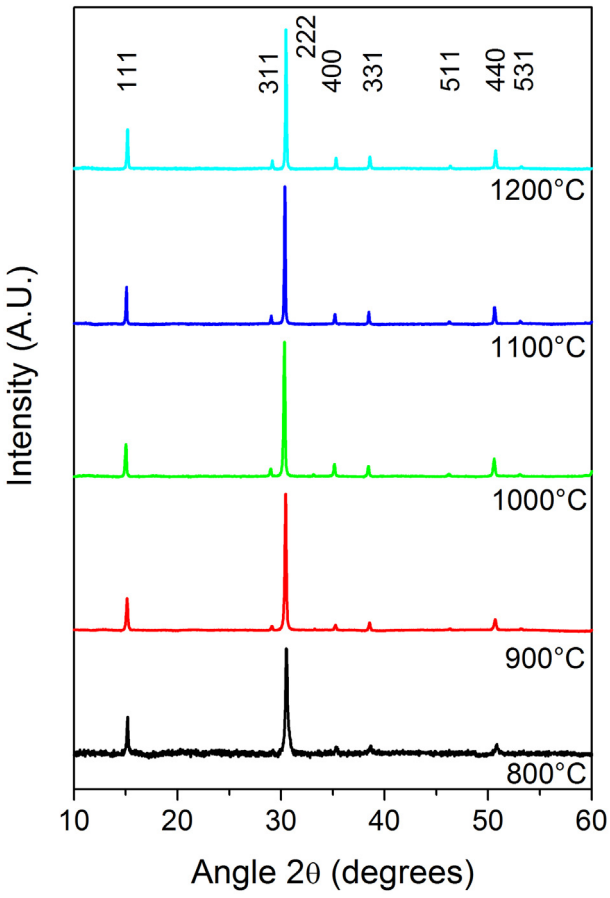


**Fig. 1.** XRD patterns of annealed films with denoted (*hkl*) indices.

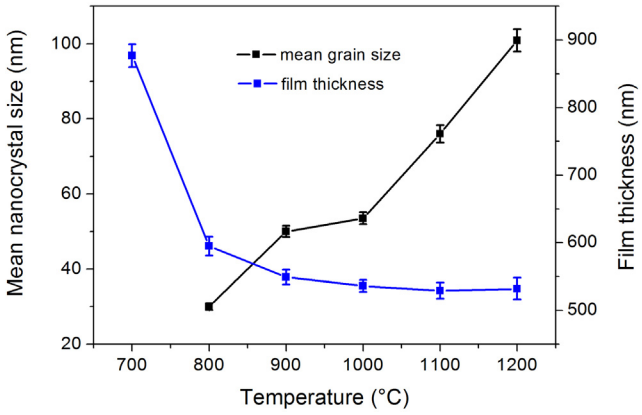


**Fig. 2.** Thermal evolution of the calculated mean nanocrystal size (left scale) and the film thickness (right scale).

to prepare both positive and negative patterns, set of ribs wider than 10 μm as well as advanced motifs, e.g. circles, numbers. The patterns were crack-free and longitudinally homogenous. Corner rounding radius of the pattern was lower than 6 μm. The lateral dimensions of the pattern remained unchanged during the annealing indicating that the volume changes accompanying the annealing were compensated only by the change in thickness. The film consisted of closely packed uniform nanocrystals with the nanocrystal size approximately 50 nm. This observation perfectly matches the nanocrystal size 53 nm calculated from XRD records.