Ceramics International 44 (2018) 9479–9483

Contents lists available at ScienceDirect

Ceramics International

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

CO_2 laser-assisted preparation of transparent $Eu_2Ti_2O_7$ thin films

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

[a] Institute of Photonics and Electronics of the Czech Academy of Sciences, Chaberská 57, 18251 Prague 8, Czech Republic
[b] Institute of Physics of Materials of the Czech Academy of Sciences, Žižkova 22, 616 62 Brno, Czech Republic
[c] Institute of Materials of the Slovak Academy of Sciences, Watsonova 47, 04353 Kosice, Slovakia

ARTICLE INFO

Keywords:
Laser processing
A. Sol-gel processes
A. Films
C. Optical properties

ABSTRACT

We present a laser-assisted preparation of transparent europium-titanate $Eu_2Ti_2O_7$ thin films with tailored structural and optical properties. We have evaluated the effects of the irradiation time on the structural and the optical properties of the films. This approach allows the preparation of nanocrystalline crack-free films and micro patterns. The amorphous thin films were prepared by a sol-gel method. The films were annealed by a CO_2 laser beam for various time intervals. The laser irradiation induced a crystallization process that resulted in the formation of $Eu_2Ti_2O_7$ nanocrystals. The nanocrystals regularly grew with increasing irradiation time reaching the size from 25 nm to 45 nm. A film of a thickness 480 nm exhibited an optical transmission of 91.9% that is close to the maximal theoretical limit. The film's refractive index at 632 nm was 2.26. A micrometric pattern was prepared by a direct laser writing followed by a wet chemical etching. Feasibility of the demonstrated approach, together with the high film's quality, and europium-titanate chemical resistivity open up many opportunities for advanced applications. The approach can be used for a preparation of protective coatings and integrated photonic devices such as planar optical waveguides and couplers.

1. Introduction

Lanthanide titanium oxides, which crystallize in the face-centered cubic pyrochlore structure with the general formula $RE_2Ti_2O_7$ (RE = rare earth element) [1], have attracted large attention of recent materials research. This family of materials has attracted huge attention for their high thermal stability, chemical resistivity, and low expansion coefficient as perspective materials for thermal barrier coatings [2]. Moreover, the local spin arrangement in the pyrochlore lattice brings phenomenal magnetic properties that strongly depend on the RE incorporated within the pyrochlore crystal lattice [3–5]. For this reason the $RE_2Ti_2O_7$ compounds have been established as key materials for spintronics [5–7]. However, the effective exploitation of these materials still has been limited because of their crystallization temperatures that are higher than 700 °C [8,9]. High crystallization temperatures prevent the possible preparation of nanocrystalline coatings on commonly used glass substrates and the effective exploitation in integrated devices. A CO_2 laser-assisted treatment can solve this challenge.

CO_2 laser treatment is a powerful method that allows a local surface heating of the materials and minimize the thermal damage to the substrate [10–12]. It has been used for micromachining of glass and ceramics materials [13], to induce a phase transformation of polycrystalline solids [13], etc. Moreover, a laser treatment has been used for the preparation of sophisticated photonics components such as integrated optical waveguides [14], long period gratings [15], etc. All introduced properties make the CO_2 laser treatment suitable for processing of nanocrystalline $RE_2Ti_2O_7$ thin films.

In this contribution, we present a CO_2 laser-assisted preparation of highly transparent nanocrystalline europium-titanate $Eu_2Ti_2O_7$ thin films. We study the effects of the annealing time on the formation and the growth of the nanocrystals. We evaluated the film's structural and optical properties. A micro pattern was prepared by a direct laser writing. The results provide fundamental information about the effect of the CO_2 laser treatment on the structural and optical properties of nanocrystalline $Eu_2Ti_2O_7$ thin films. The demonstrated approach allows to preparation of highly transparent films and micrometric patterns that are suitable for a preparation of protective coatings and advanced spintronic devices.

2. Materials and methods

2.1. Preparation of thin films

The starting sol, that was used to thin film deposition, was prepared

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

https://doi.org/10.1016/j.ceramint.2018.02.165
Received 2 February 2018; Received in revised form 20 February 2018; Accepted 20 February 2018
Available online 21 February 2018

by an already published approach [16]. Five layers were subsequently dip-coated onto a silica glass substrate (Technical glass products, USA) by a withdrawing speed 150 mm min^{-1}. Each layer was densified in a rapid thermal annealing furnace AccuThermo AW410 (Allwin21 corporation) at 550 °C for 60 s under an oxygen flow of 5 l·min^{-1} and a heating rate of 10 °C s^{-1}.

The densified films were irradiated by a continuous CO_2 laser (SYNRAD 48–1 S) emitting at 10.6 μm. A laser beam was expanded to a 5 mm circular spot, a power density of the laser beam was around 20 mW mm^2 and the densified films were irradiated for different time. Alternatively, the laser beam was focused to a 0.5 mm circular spot and the densified films were moved in the beam by means of a computer-controlled X–Y linear translation stage to write a pattern. The stage velocity was 4 mm s^{-1}. The irradiated films were alternatively exposed to a 10% water solution of hydrofluoric acid for 300 s to remove the amorphous fraction.

2.2. Characterization techniques

X-ray diffraction (XRD) analyses were obtained 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.

The steady-state luminescence spectra were recorded on a Fluorolog 3 (Horiba Jobin-Yvon) spectrometer equipped with a photomultiplier. The emission spectra were recorded from 570 to 720 nm with a step of 0.5 nm and a slit of 1 nm under the excitation at 394 nm with an excitation slit of 5 nm. The integration time was 0.5 s.

UV–VIS transmission spectra were recorded on a spectrometer Lambda EZ 210 (Perkin-Elmer). The refractive indices were calculated from the transmission spectra by Swanepoel's method for weak absorbing films. According to this method the refractive index n was calculated from the relationship [17]:

$$n = \left\{\left[n_{sub}\bullet\frac{T_M - T_m}{T_M\bullet T_m} - \frac{n_{sub}^2+1}{2}\right] + \left[n_{sub}\bullet\frac{T_M - T_m}{T_M\bullet T_m} - \frac{n_{sub}^2+1}{2}\right]^{\frac{1}{2}}\right\}^{\frac{1}{2}}, \quad (1)$$

where T_M represents the transmittance maxima and T_m represents the transmittance minima of the interference pattern, n_{sub} is the refractive index of the substrate which is equal to 1.457 for fused silica glass [17].

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 sample charging. The thickness and the surface profiles of the samples were measured on an optical profilometer NewView 7300 (Zygo).

3. Results and discussion

3.1. Structural characterizations of the films

The effect of the laser annealing on the nanocrystal growth is shown in Fig. 1. The densified film was fully amorphous as can be concluded from the absence of an X-ray diffraction pattern. Broad peaks located between 15° and 40° corresponded to the background signal of the silica substrate. The laser annealing of the amorphous films induced the crystallization of $Eu_2Ti_2O_7$ and caused a regular growth of the nanocrystals. Formed nanocrystals provided the diffraction pattern typical for $Eu_2Ti_2O_7$ pyrochlore structure. The diffraction peaks became more intensive and better pronounced with prolonged irradiation time. The absence of the alternative phases; such as Eu_2O_3 or TiO_2; confirmed the high purity of the nanocrystals.

Fig. 2 shows the effect of the laser annealing on the luminescence

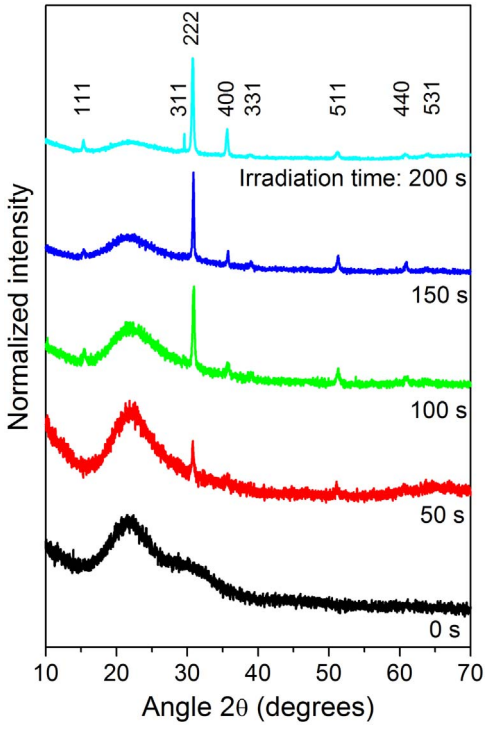

Fig. 1. XRD patterns of irradiated samples with denoted (*hkl*) indices.

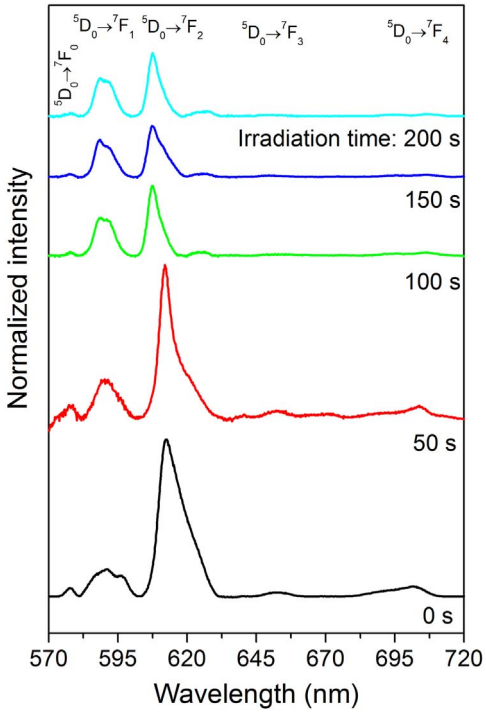

Fig. 2. Emission spectra of the laser-annealed films normalized to the intensity of the MD peak at 592 nm.

properties of the films. The particular electronic transitions of Eu^{3+} ions were identified according to the literature [6,18]. Densified film exhibited broad peak at 578 nm, which corresponds to $^5D_0\rightarrow{}^7F_0$ symmetry forbidden transition. The intensity of the emission peak at 614 nm, which corresponds to the electric-dipole allowed $^5D_0\rightarrow{}^7F_2$ (ED) transition, was several times higher than the intensity of the emission peak at 592 nm, which corresponds to the magnetic-dipole allowed $^5D_0\rightarrow{}^7F_1$ (MD) transition. The intensities of the peaks located