



Erbium-doped yttria thin films prepared by metal organic decomposition for up-conversion

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ABSTRACT

Er:Y₂O₃ thin films have been obtained by spin coating process. Precursor solutions were prepared using nitrates as metal precursors and water as solvent. Citric, malic, and lactic acids were used as complexant. Investigations on resin compositions and on their coating parameters have been made, leading to crack-free thin films with citric and malic acids after direct deposition under standard room conditions (temperature, pressure and atmosphere). The films are homogeneous with a low root mean square roughness, less than 2.5 nm. We demonstrated that the nature of the carboxylic acid is the key point to obtain high quality thin films on silicon substrates from 20 nm up to 230 nm thick, while the film porosity is related to the number of carbon in the acid molecule. All films exhibit up-conversion luminescence in the near infrared and in the visible range, under 1.54 μm laser excitation. Furthermore, the up-conversion luminescence intensity increases with the applied annealing temperature on the films, due to an improvement of their crystallinity and to the total decomposition of organics.

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1. Introduction

Yttrium oxide has attracted much attention since many years due to a panel of interesting physical properties for several applications (thermal coating, electronics, optics). In particular, for optics, this material is attractive because of its high band gap value (>5.6 eV) providing transparency in a broad spectral range (from 0.23 up to 8 μm), and its high refractive index ($n \sim 1.9$) [1]. Moreover Y₂O₃, with a thermal conductivity ($K = 0.33 \text{ W cm}^{-1} \text{ K}^{-1}$) higher than that of YAG ($K = 0.10\text{--}0.14 \text{ W m}^{-1} \text{ K}^{-1}$) [2,3] and a thermal expansion coefficient similar to that of YAG, is an attractive material for high power lasers. Furthermore, Y³⁺ has the same charge, a comparable ionic radius and similar chemical properties than most of trivalent rare earth (RE) ions, which enable to achieve high doping level as $6.10^{21} \text{ ions}\cdot\text{cm}^{-3}$, which is a great advantage in rare earth spectroscopy [4]. In addition, Y₂O₃ exhibits the lowest phonon cut-off frequency ($\approx 600 \text{ cm}^{-1}$) among oxides, thus non radiative de-excitation processes of RE excited

states by multiphonon relaxation are minimized. Considering this property and the effect of the refractive index on the local field, which favors radiative emission of RE ions in this host, the quantum efficiency of their luminescence is usually high. All these properties of low non radiative relaxation, long lifetimes of intermediate energy levels and good thermal properties, are beneficial to achieve efficient up-conversion [5].

Up-conversion is a non linear process which can have several applications, but the final aim of this study is to integrate RE:Y₂O₃ layers as up-converters in third generation solar cells [6]. In this scheme, the active film is placed behind a bifacial solar cell and converts sub-band-gap radiation transmitted by the cell into higher wavelengths, which can be absorbed by the cell. This concept has been widely demonstrated with bulk materials, but for a real application, up-converters must be used as thin film and this is the motivation of this work.

Several papers reporting the preparation of Y₂O₃ films can be found in the literature. Indeed, Y₂O₃ thin films have been deposited by physical vapor deposition [7], pulsed laser deposition [8], sputtering [9], atomic layer epitaxy [10,11], electrochemistry [12] and sol-gel [13]. Among these methods, the sol-gel route offers several advantages such as its versatility that is associated to low cost techniques of coating and easy processing. Nevertheless, the main drawbacks of sol-gel approach remain the use of highly reactive precursors (as alkoxides), making delicate the control of hydrolysis and condensation reactions. The use of yttrium alkoxide requires working under controlled atmosphere and the use of

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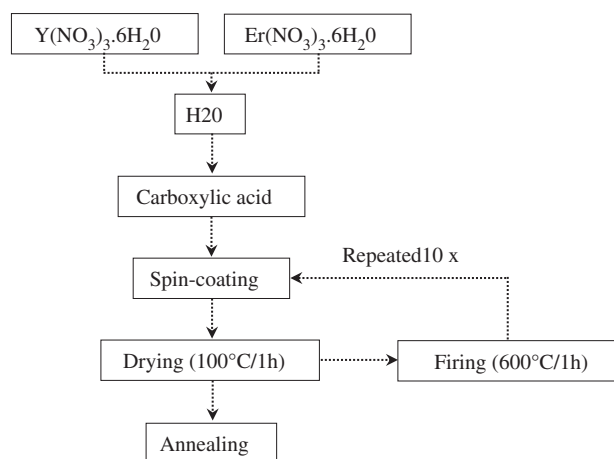


Fig. 1. Flow scheme of synthesis procedure of $Y_{1.98}O_3:Er_{0.02}$ thin films (multilayer).

non-aqueous solutions [14,15]. Another route providing the same advantages than sol-gel techniques is the metalorganic decomposition method [16]. This technique involves the coating of the substrate, directly by the solution of the metalorganic compound of the desired elements. The main challenge, for this method is the control of the solution viscosity, which generally involves the addition of other chemicals.

In this paper, we report one preparation method, based on the metal organic approach using a simple wet chemical route in aqueous solutions. Our method involves only three basic components: the metal salt, a complexant, and the solvent. This method allows us to prepare high quality polycrystalline Y_2O_3 thin films. Films reported here exhibit up-conversion property. The use of water as solvent presents several advantages as making the syntheses not only much easier, but also safer and environmentally friendly [17–19]. With this method, resin preparation and film deposition are performed at room temperature and under air atmosphere. Our method is based on the metal organic decomposition of different yttrium complexes and thin films are deposited by spin-coating. Particular attention has been directed towards the parameters determining the quality (morphology, optical properties) of the resulting thin films. Finally, promising up-conversion results are presented.

2. Experimental section

2.1. Film preparation

Initial aqueous solutions were prepared using yttrium and erbium nitrates as metal precursors and different carboxylic acids as complexant: malic, lactic and citric acids, noted as MA, LA and CA, respectively. Appropriate composition of yttrium and erbium nitrates (3 mg) (99.9%, Alfa Aesar) was mixed and dissolved in 4.5 ml of 30 M Ω deionized water (Solution A). Carboxylic acids were dissolved separately in 9 ml of water (Solution B). After the total dissolution

of precursors, solution B was added dropwise to solution A under stirring, and kept stirred 2 h more after the end of mixing to obtain a transparent solution. The as-prepared solutions were then aged at least 24 h at room temperature without stirring. Finally, these initial solutions, stable over several months, were prepared with all carboxylic acids and then filtered through 0.2 μ m filter syringes just before deposition.

<100> silicon wafers were used as substrates. After cleaning with RBS25 detergent in an ultrasonic bath and rinsing with water and acetone (18 M Ω resistivity), the substrates were plunged in a NaOH (1 M) solution for 1 min, then rinsed again under ultrasonic bath, firstly with water and secondly with 2-propanol. Then, the substrates are finally dried under a dry nitrogen flow. The treatment with NaOH step is essential because the wetting property of aqueous solution on silicon substrates and the final quality of films depend mainly on it. Indeed, the soda solution dissolves the native SiO_2 layer allowing the removal of all contaminations at the surface of the substrates and inducing thus a better wettability of the resins [20,21]. Indeed, the contact angles of water drops on substrates without this alkali treatment are around 30°, while those treated with soda are lower than 10°. This indicates a significant increase of substrate hydrophilicity due to the formation of silanol groups (Si–OH) on silicon surfaces.

1 at.% Erbium-doped yttria thin films were deposited at room temperature by spin-coating (table-top SPIN150™-NNP processor). As-deposited thin films were then dried at 100 °C during 1 h and calcinated at 600 °C also during 1 h under air atmosphere, to decompose organics. These steps of deposition–drying–calcination were repeated until the targeted thickness of the resulting multilayer was achieved, around 10 layers. The final annealing temperature of the multilayer was tested from 600 °C to 900 °C for 2 h in agreement with previous works [22]. The overall coating procedure is summarized in Fig. 1.

2.2. Characterizations

The resin viscosities were measured with a LOW SHEAR 30 rheometer. Grazing Incidence X-ray Diffraction (GIXRD) experiment was carried out on a PaNalytical apparatus (Empyrean) with a copper anticathode at the wavelength of $CuK\alpha_1 = 1.54 \text{ \AA}$. The used grazing incidence angle was 0.5° and diffractograms were recorded between $2\theta = 20^\circ$ and $2\theta = 90^\circ$. Compositions of yttria thin films were determined by secondary ion mass spectroscopy (SIMS) measurements. SIMS were made on IMS 3f camera, using a Cs^+ primary beam with a primary acceleration voltage of 10 kV and a secondary voltage of 5 kV. Film morphology was investigated by scanning electron microscopy (SEM, HITACHI TM 1000, with an operating voltage of 15 kV and Zeiss Supra 55, with an operating voltage of 5 kV) and by atomic force microscopy (AFM, Veeco-Brucker DI 3100, tapping mode). The film thickness was measured by a Dektak profilometer. Optical characterizations were performed with a confocal microscope with an objective of 0.55 numerical apertures. The excitation was provided by a 1.5 μ m fiber laser diode, while the signal, dispersed through a SP2300 monochromator (Princeton Instrument), was detected by a SPEC-10 (eXelon) type CCD camera. A dichroic filter (Thorlabs DMLP 1180) was used to collect all the up-converted luminescence without collecting the incident excitation.

3. Results and discussions

The spin-coating process involves centrifugal forces for spreading the solution initially deposited at the center of a flat substrate. In this process, there are several main parameters to control the quality and final thickness of thin films [23]. Among them, one of the key parameters is the viscosity η of the resin. Indeed, for high η values, no film of good quality can be obtained while for low η values, only film with a low thickness can be deposited. Deposition related parameters as resin volume, acceleration, rotation speed and processing

Table 1
Viscosity of the prepared solutions.

Samples	Viscosity (cPo)
Water	0.85
Water + LA	1
Water + MA	1
Water + CA	1.1
Water + nitrates	1.2
Water + LA + nitrates	1.3
Water + MA + nitrates	1.4
Water + CA + nitrates	1.5

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