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ABSTRACT

We report here a method to enhance light extraction from the top face of a TiO_2 waveguide doped with a molecular emitter. Sol-gel TiO_2 surface is patterned by a 2D photonic crystal with a 400-nm period and a 40-nm depth, as verified by Scanning Electron Microscopy and Atomic Force Microscopy. We evidence that light emitted in the TiO_2 layer is efficiently extracted by the surface patterning and quantify the extraction enhancement by measuring the emission spectra as a function of the emission angle. We measured an enhancement factor of 3 within 50° off normal.

Keywords: Soft nanoimprint lithography, sol-gel chemistry, light extraction, photonic crystal

1. INTRODUCTION

Transparent thin films are commonly investigated for the development of waveguides [1,2] or the elaboration of devices for display or lighting applications [3]. The characteristics that are required for these applications are very different in terms of light guidance: in the case of a waveguide, one wants to keep the light trapped inside the film as far as possible, whereas in the case of luminescent devices, one wants the light to be rapidly extracted from the top face of the film.
The issue of light extraction in guiding films is commonly tackled to enhance light outcoupling in LEDs [4] or in OLEDs [5] and thus to obtain higher external quantum efficiency of the device. To achieve this, different approaches are studied, such as the incorporation of scattering centers, the addition of roughness or the regular patterning of the surface.

In this study, we investigate the influence of periodic surface patterning, also called photonic crystal (PhC) onto light extraction in luminescent TiO_2 sol-gel waveguide. Sol-gel chemistry allows preparation of high optical quality films and surface patterning by Soft Nanoimprint Lithography [6]. Moreover, the films synthesized by this method can incorporate a large variety of luminescent species, such as organic dyes, inorganic clusters, rare-earth chelates or even luminescent nanoparticles.
The system under study, sketched on Figure 1, consists of a 200-nm thick TiO_2 film doped with a luminescent europium chelate, deposited onto a glass substrate. On the top of this film is deposited an undoped TiO_2 film which has been patterned for light extraction.
This system is well adapted to this study for several reasons:

(1) Our TiO_2 film makes a good optical waveguide [2]. Indeed, due to the difference in refractive index between TiO_2 (n~1.7) and the substrate (n~1.5), guided modes exist. In order to simplify the study, we set the thickness of the film so that a single guided mode is present in the whole structure. The TiO_2 is kept amorphous as

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crystallization would undoubtedly induce grain boundaries whose scattering would rapidly jeopardize the guided mode.

(2) The luminescent chelate offers the advantage of being a molecular species and thus is easily incorporated into the TiO_2 film without forming any clustering or inducing any scattering. In addition, it is highly luminescent around 620 nm, with a 25% quantum yield in solution and a large absorption cross-section at 370 nm, corresponding to the excitation in the ligand LUMO states. The large Stokes shift allows avoiding any reabsorption effects. Its main drawback lies in the fact that it is not very photostable, in particular in TiO_2.

(3) An additional TiO_2 sublayer was added in order to perform surface patterning without modifying the local concentration of emitters, avoiding thus any perturbation at the very root of the luminescence.

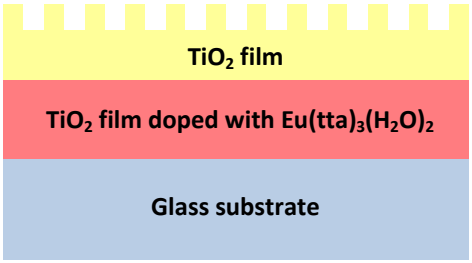

Figure 1. Scheme of the structure under study: A TiO_2 sol-gel film doped with europium chelate has been deposited onto a glass substrate. An additional layer of TiO_2 has been spin-coated onto the luminescent structure and patterned by soft nano-imprint lithography.

2. EXPERIMENTAL SECTION

2.1. Synthesis of TiO_2 thin film doped with $Eu(tta)_3(H_2O)_2$

Titania sol was prepared by mixing 18 mL of titanium (IV) butoxide with 9.8 mL of butanol. 27.3 mL of acetic acid was added and the mixture was heated at 50°C. After stirring for 30 minutes, the solution was cooled to 0°C for 1 hour. 8.9 mL of DI water and 37.6 mL of ethanol were mixed together and slowly added to the cold solution. The resulting mixture was heated at 50°C for 1 hour and finally filtered with a 0.22-µm porous membrane.

Europium chelate $Eu(tta)_3(H_2O)_2$ was synthesized according to C.R. De Silva *et al.* [7]. As it is soluble in ethanol, it s easily incorporated into the TiO_2 sol with a concentration of 20 g/L.

The TiO_2 sol doped with $Eu(tta)_3(H_2O)_2$ was deposited onto a glass substrate previously cleaned by UV-Ozone by spin-coating at a speed of 2000 rpm for 30s.

The obtained film was dried at 110°C for 10 minutes. This heat treatment allows completing the condensation of the TiO_2 without crystallizing it.

2.2. Synthesis of TiO_2 sublayer

A TiO_2 sol was prepared by mixing 10 mL of titanium (IV) butoxide with 7 mL of acetylacetone. The mixture was stirred for 15 minutes. Then, 8mL of isopropanol and 240 µL of acetic acid were mixed together and added drop by drop to the titanium precursor solution. After 1 hour stirring, the sol was filtered at 0.45-µm porous membrane.

The TiO_2 sol was diluted twice in isopropanol and deposited by spin-coating at 3000 rpm for 30 s.

2.3. Surface patterning

Before the TiO_2 sublayer condensates, a polydimethylsiloxane (PDMS) stamp, previously prepared from a silicon master and treated by an anti-adhesive agent (TriMethylChloroSilane), was applied at the surface of the film. The whole system was placed into a NXR2500 imprinter from Nanonex for 5 minutes. During this step, a pressure of 20 psi was applied onto the film. This latter was also heated at 110°C so that the TiO_2 condensates and retains the structure of the mold after removal of the mould.

The structure of the mold chosen for this study is a 2D square photonic crystal, with a period of 400 nm, a depth of 90 nm and a filling factor of 0.26.

2.4. Structural characterizations

Scanning Electron Microscopy (FEG-SEM Hitachi 4800) was performed onto the patterned films in order to evaluate the reproducibility of the patterning. It was operated at 3.0 kV to minimize charging.
Atomic Force Microscopy was also carried out.

2.5. Optical characterizations

In order to characterize the angular dependence of the film emission, an optical experiment was set up: the sample and the excitation source (a 376-nm fibered laser) were placed onto a rotation stage and the film emission was collected and focused onto a spectrometer (QE65000 Ocean Optics) for each position of the sample. The emission spectra recorded for each detection angle θ were gathered together in a luminescence map. The normal direction is defined for θ=90°.
Quantitative comparison of the intensity of light extracted from the top and bottom faces of a patterned film and of an unpatterned film was performed using an integrating sphere (Fluoromax-4, Jobin-Yvon). Films were placed inside the integrating sphere and their luminescence was collected between 550 and 700 nm. In order to collect only the emission coming out from the faces and not from the edges, the film edges were carefully blackened.

3. STRUCTURAL CHARACTERIZATION OF SURFACE PATTERNING

At normal incidence, the diffracted light wavelength λ is related to the mold period a by the relation: $\lambda = a\, n_{eff}$ where n_{eff} is the effective index of the guided mode. This effective index n_{eff} is calculated using a free software: n_{eff}=1.54 at 620 nm [8]. In order to extract light emitted by the europium chelate (main peak at λ=620 nm) in the near normal direction, we chose to use a mold with a period of 400 nm (620/400=1.55).

Figure 2 shows the top view of a patterned TiO_2 film. Over large distances, the 2-dimensional structure has been reproduced with high fidelity. From the SEM image, the period is measured to be a=400 nm, corresponding to the period of the mold.

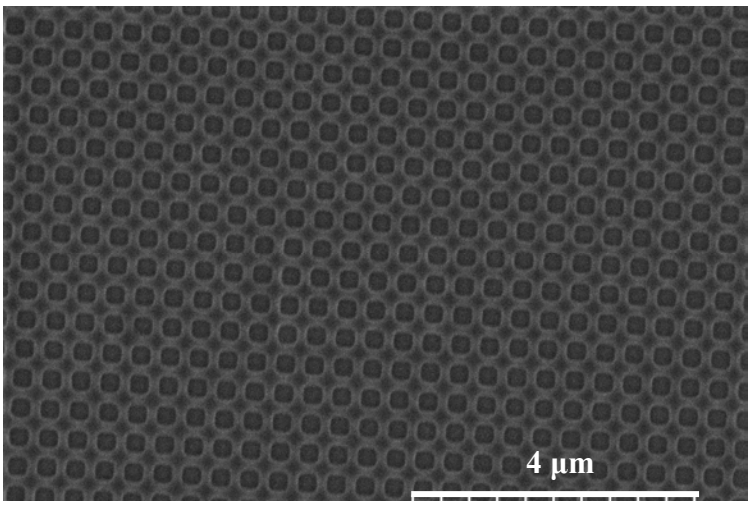

Figure 2. SEM image of the 2-dimensional surface pattern of a TiO_2 sol-gel film.

Atomic Force Microscopy allows a reliable measurement of the pattern depth. With the sol concentration and the spin-coating conditions mentioned in the Experimental Section, a depth of 40±2 nm was measured (Figure 3). It is shallower than the depth of the mold (90 nm), suggesting that the TiO_2 sol does not completely fill the mold. By changing the sol

concentration, it should be possible to increase the pattern depth and perfectly reproduce the mold parameters but this issue has not been addressed in the present study.

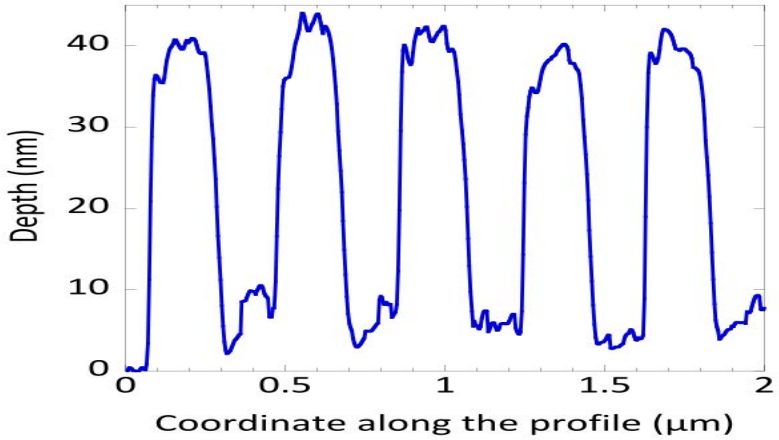

Figure 3. AFM profile of the patterned TiO_2 film along a photonic crystal main axis.

4. INCREASE OF LIGHT EXTRACTION BY SURFACE PATTERNING

4.1 Qualitative analysis

By illuminating a film by UV light (312 nm) we observe that the patterned area appears brighter than the unpatterned area (Figure 4). Note that a homogenous amount of emitters has been introduced in the whole film. This observation, though qualitative, evidences the efficiency of the surface patterning on light extraction. We checked elsewhere that UV light excitation is not noticeably affected in our setup.

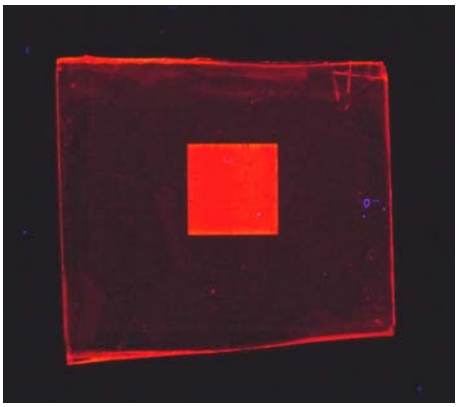

Figure 4. Photo of a TiO_2 film doped with europium chelate under 312-nm illumination. The center of the film has been patterned on a 1 cm by 1 cm square. A constant concentration of chelate is present across the whole film.

4.2 Quantitative measurements

In order to gain more quantitative insights on the effect of the PhC, angular emission measurements have been performed, both on an unpatterned film and on a patterned film. The luminescence maps thus obtained are presented on

Figure 4 (a) and (b) respectively. They correspond to the emission spectra as a function of the detection angle θ (normal is at 90°).

For the unpatterned film, the emission spectrum of the film remains unchanged whatever the detection angle θ. The obtained spectrum, reported on Figure 4(c), is characteristic from Eu^{3+} emission, with an intense peak centered at 620 nm corresponding the $^5D_0$-$^7F_2$ transition. The map has been recorded from θ=140° to θ=40° with an acquisition time of 1s, a dead time of 1s and a 0.2° step, i.e. over 17 minutes. As the europium chelate is not photostable when incorporated into TiO_2, its emission intensity decreases with time. It explains why the emission intensity decreases from θ=140° to θ=40°, with a steady exponential decay that can be therefore taken into account when it comes to normalization.

For the patterned area, the luminescence map, recorded in the same conditions, has a very different aspect, with two narrow tilted lines that cross around θ=90° and a broad bowed band. All of these features correspond to light that is diffracted by the PhC as analyzed by A. Revaux *et al.* [9]. The emission spectrum of Eu^{3+} depends on the detection angle θ (Figure 4(d)) and is modulated by the diffraction of the PhC.

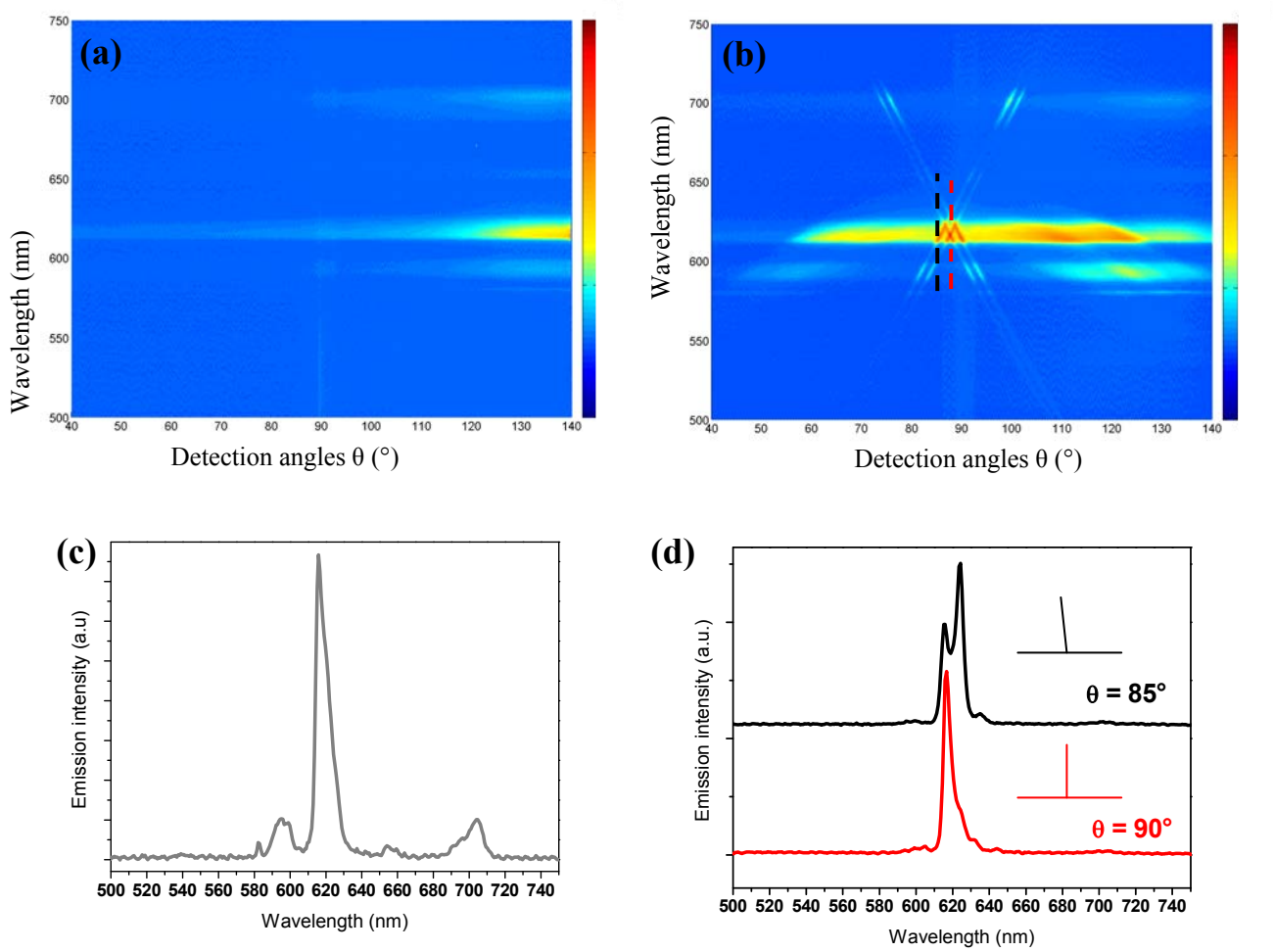

Figure 5. (a) and (b) Luminescence maps corresponding to the emission spectra detected at different angle positions for the unpatterned and patterned areas respectively. The color lookup table represents the emission intensity. Dashed lines refer to spectra in (d). (c) Emission spectrum of the film obtained whatever the detection angle, on the unpatterned area. (d) Emission spectra of the patterned film for specific detection angles (θ=85° and θ=90°), showing that the emission spectrum of Eu^{3+} is modulated by the PhC diffraction.

An extraction enhancement factor has been evaluated by integrating the emission intensity in the 600-620 nm range, over θ=40° to θ=140° (i.e. normal ±50°), for the patterned film and the unpatterned film, and by calculating the ratio. As the two maps were recorded over the same duration, the intensity decrease due to the lack of photostability of the chelate can be considered as identical, and it can be well mitigated for quantitative assessment. An extraction enhancement factor of 3 is found, meaning that, thanks to the surface patterning, three times more light is extracted from the TiO_2 waveguide.

In order to confirm this value, we also proceeded to a measurement in the 500-750 nm range in an integrating sphere. This measurement corresponds to the light collection over θ=0° to θ=180° (normal±90°) on both faces since the sample lies completely inside the sphere in our geometry. Note that the edges of the patterned and unpatterned films were blackened, so that only the light coming out of the films by the top face and by the bottom face was analyzed. The comparison between the patterned film and the unpatterned one shows that the patterned film generates twice more light from the faces. This value is consistent with the value found by integrating the signal on the luminescence maps (the specific setup of [9] also introduces a small difference with a measurement in a truly conical solid angle of 50°, but of quite modest consequence). Our analysis indicates that the PhC extraction enhancement is more pronounced toward the top than the bottom, due to the detailed diffraction processes, and therefore, we believe that the difference between these two measurements mainly comes from the fact that, in an integrating sphere, the signal coming from both the top and the bottom faces is collected, whereas in the measurement based on the luminescence maps, only the signal emitted from the top face is collected.

5. CONCLUSIONS

Successful 2D surface patterning was performed onto TiO_2 sol-gel films, enhancing light extraction from the top face of the films. High fidelity has been obtained between the mold period and the period of the film pattern and no cracks were observed. Moreover, regular pattern depth was obtained over large distances. Thanks to a precise angular measurement of the extracted light, the signature of the surface photonic crystal has been observed and quantitative measurements could be carried. An extraction enhancement factor of 3 has been determined when considering emission within an angle of 50° off normal.

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