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Room-temperature nanoimprinting on metallo-organic complexes

Elisa Mele, Dario Pisignano,^{a)} Marco Mazzeo, Luana Persano, Giuseppe Gigli, and Roberto Cingolani

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We apply room-temperature nanoimprint lithography to rare-earth metallo-organic complexes, for patterning 600 nm period gratings onto europium-based 612 nm light-emitting compounds. After patterning, an increase of up to 6.2 times of the integrated photoluminescence emitted around $\Theta=35^\circ$ was observed, resulting from the combination of the effective Bragg scattering induced by the printed grating, with the very narrow-linewidth emission of the metallo-organic complexes. These results are quite promising for the realization of nanoimprinted rare-earth-based optoelectronic devices, such as light-emitting diodes and displays, and distributed feedback elements. © 2004 American Vacuum Society. [DOI: 10.1116/1.1714952]

I. INTRODUCTION

One promising and effective solution to the problem of engineering and controlling the optical properties of light-emitting materials is represented by the use of photonic crystals (PhCs), namely periodic dielectric structures able to favor or to prevent the propagation of light at certain frequencies along certain directions.^{1,2} In particular, the application of PhCs to low-cost organic compounds, allowing excellent luminescence performances and easy synthesis and processing routes,³ could be strategic in modern optoelectronics technology. Among different proposed fabrication methods of organic-based PhCs structures, including soft,⁴ electron-beam,⁵ and optical lithography,^{6,7} a cheap and powerful technique is nanoimprinting lithography (NIL), allowing very high throughput and resolution.⁸

The conventional imprinting technology consists of the compression molding of thermoplastic polymers. A mold with an engraved pattern is mechanically pressed onto a substrate coated with a polymeric material. Afterward, the system is heated above the glass transition temperature of the polymer, above which the viscosity strongly decreases. This allows the polymer to conform with the mold pattern. After pressing and subsequent cooling below the glass transition temperature, the mold is removed, and a negative replica of the initial pattern remains on the target. To date, 10 nm diameter and 40 nm period holes have been fabricated in polymeric films by NIL.⁹

However, the requirement of the employed molecules to be thermoplastic in nature limits the use of NIL and prevents its use with many low-molar-mass light-emitting molecules. Moreover, when hot embossing is applied to active organic materials, it has to be carried out in a vacuum chamber or in nitrogen atmosphere to avoid the degradation of the optical and electrical properties of the compounds, mainly induced by oxygen incorporation and substitution at high temperature.¹⁰ Room-temperature nanoimprinting (RT-NIL),

initially proposed as alternative manufacturing techniques for patterning thermoplastic polymers,¹¹ allows one to fully overcome these drawbacks, as it exploits only an applied pressure to transfer the pattern, thus being suitable for processing of nonthermoplastic compounds under an uncontrolled atmosphere.

In this work, we apply RT-NIL to metallo-organic complexes, patterning films of europium (Eu)-based compounds with periodic 300 nm features, suitable for the realization of PhCs and distributed feedback optical devices.¹² Among rare-earth complexes, which are characterized by high photoluminescent (PL) efficiency, η_{PL} , and sharp emission bands,^{3,13} (Eu)-based complexes appear very attractive due to their red emission, in view of their wide potential applications in full-color displays and electrically pumped lasers.^{13–15} After patterning, we observed well-defined features, conforming the geometry of the mold. More important, an increase up to 6.2 times of the luminescence emitted around $\Theta=35^\circ$ was observed, resulting from the combination of effective Bragg scattering and the very narrow-linewidth emission of the metallo-organic complexes. These results can be very useful for improving the performances of optoelectronic devices based on rare-earth emitting compounds.

II. EXPERIMENT

Our lithographic process is schematized in Fig. 1(a). The Eu-based compounds, namely the low-molar-mass molecules tris(benzoylacetonato)-mono(phenanthroline)-europium(III) (No. 1) and tris(dibenzoylmethane)-mono(phenanthroline)europium(III) (No. 2) [molecular structures are displayed in Figs. 2(a) and 2(b), respectively] were purchased from H. W. Sands Corp. (FL) and used as received. 3.6×10^{-2} M chloroform solutions were spincoated at 1500 rpm onto Corning glass substrates, thus achieving uniform 300 nm thick films. Master patterns with parallel grooves of period of 600 nm and duty-cycle 50% were first fabricated on silicon by electron-beam lithography by a Raith (Germany) Elphy Plus pattern generator controlling a Leica (Ger-

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FIG. 3. AFM two-dimensional view of the pattern transfer into compound No. 1 (a) and the corresponding cross section (b).

film from the substrate. Molecules of low-molecular weight generally need low pressure to be imprinted. We adopted pressures comprised between 100 and 600 atm, finding that an incomplete pattern transfer occurs with pressure values below 300 atm, and that pressures higher than 500 atm determine a loss of adhesion between the organic material and the glass substrate. The process duration was varied between 30 min and 8 h. An imprinting time of 2 h was chosen to achieve a complete pattern transfer with an applied pressure of 400 atm.

The plan view and the cross section of a 600 nm period Eu-based grating (compound No. 1), imaged by AFM, is displayed in Fig. 3, showing a well-defined pattern faithfully reproducing the periodicity of the master. The depth of the imprinted grooves is (170 ± 4) nm. The achieved resolution depends on the starting master, which suggests the possibility of fabricating 100 nm features onto rare-earth compounds. Identical results were obtained patterning compound No. 2.

In order to assess the influence of patterning on the emission properties of the metallo-organic complexes, we investigated the PL from both patterned and unpatterned samples as a function of the collection angle, Θ . The emission from compound No. 1 ($\eta_{\text{PL}} = 12\%$) at $\Theta = 35^\circ$ is shown in Fig. 4 (solid line). The narrow PL from rare-earth complexes originates from the excitation of the S_1 singlet state of the surrounding organic ligands, whose energy is first transferred to the ligand triplet state, T_1 , via intersystem crossing, and then to the central metal ion.^{18,19} In particular, the emission from Eu-based complexes is peaked at 612 nm, and involves electrons associated with inner f orbital of the central rare-earth

FIG. 4. PL spectra at an emission polar angle, $\Theta = 35^\circ$, for a patterned (dotted line) and an unpatterned (solid line) Eu-based film. Inset: Angular dependence of the integrated PL emission for a patterned (empty circles) and unpatterned sample (solid circles).

metal ions and correspond to the $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} .¹³ It has been exploited for realizing highly efficient and bright light-emitting devices,^{18,20} reaching an external quantum efficiency as high as 2.1% and a luminance of 1670 cd/m^2 .¹⁸

Interestingly, the integrated emission from our Eu-based patterned gratings at $\Theta = 35^\circ$ is more than six times higher than that of the untextured sample (dotted line in Fig. 4). The occurrence of a strong output mechanism from the grating around this emission angle is confirmed by the angular distribution of the integrated PL intensity, I , normalized to the normal intensity, I_0 (inset of Fig. 4). As opposed to the unpatterned sample, the ratio I/I_0 of the corrugated films exhibits a remarkable increment for Θ comprised between 25° and 45° , being maximum at $\Theta = 35^\circ$. Compound No. 2 exhibits a similar behavior.

The insertion of a one-dimensional wavelength-scale periodic nanostructure into light-emitting films strongly enhances the forward output from the active compound, because photons are preferentially scattered along certain directions, instead of being guided along the slab.^{6,7} The imposed grating enables the light trapped in waveguide modes to be Bragg scattered out of the film along the forward direction, reducing the self-absorption within the organic slab. The emission angle of the output wavelength, λ , is related to the cavity geometry by the relation:

$$\frac{2\pi}{\lambda} \sin \Theta = \pm \frac{2\pi n_{\text{eff}}}{\Lambda} \pm m \frac{2\pi}{\Lambda}, \quad (1)$$

where n_{eff} is the effective refractive index of the waveguided mode, Λ is the grating period, and m is an integer. The scattering process is therefore governed by the coupling condition of the guided photons to the free radiation, namely by the conservation of the in-plane component of the wave vector of the output light, $k_0 = \pm 2\pi/\lambda$, and of the guided mode, $k_g = \pm 2\pi n_{\text{eff}}/\Lambda$, by the Bragg vector (PhC reciprocal lattice vector), $G = 2\pi/\Lambda$. By means of this radiation coupling to free radiation, the use of planar PhCs within both inorganic²¹ and organic^{6,7} light-emitting diodes can also be exploited to

increase the device forward luminance. According to Eq. (1), the guided radiation within our Eu-based organic slab experiences an effective refractive index of about 1.6.

For each value of Θ , the Bragg scattering from patterned gratings generally gives rise to one or two evident peaks, superimposed to the broad luminescence spectra of light-emitting organic compounds.⁷ For our printed gratings, these extra peaks have a linewidth up to 50 nm, as we could establish by previous RT-NIL experiments with the same masters, onto organic dyes compounds with broad emission. In the case of the Eu-based complexes, due to their very narrow emission band, the printed corrugation results therefore in an enhancement of the *whole* PL spectrum for Θ around 35°. This can be very important in employing rare-earth metallo-organic complexes in optoelectronic devices, in controlling the emission directionality, and in enhancing the light output.

IV. CONCLUSION

We have demonstrated that RT-NIL is suitable for patterning rare-earth-based metallo-organic complexes, by transferring well defined 600 nm period gratings onto Eu-based light-emitting films. The output light emitted at Θ around 35° is enhanced by more than six times with respect to the unpatterned samples, due to the Bragg scattering induced by the printed gratings. These results open the way to the realization of rare-earth-based printed optoelectronic devices, like textured light-emitting diodes and distributed feedback microcavities, and are very promising also in view of the possibility of employing rare-earth complexes emitting in the infrared, such as Nd³⁺ ($\lambda=1.34\ \mu\text{m}$)- and Er³⁺ ($\lambda=1.53\ \mu\text{m}$)-based compounds, for application in telecommunications.

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