Microelectronic Engineering 87 (2010) 1367–1369

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Nanoimprinted plasmonic crystals for light extraction applications

V. Reboud [a,*], N. Kehagias [a], T. Kehoe [a], G. Leveque [b], C. Mavidis [c], M. Kafesaki [c,d], C.M. Sotomayor Torres [a,e]

[a] Catalan Institute of Nanotechnology, Campus de Bellaterra, Edifici CM7, ES, 08193 Barcelona, Spain
[b] Tyndall National Institute, University College Cork, Lee Maltings, Cork, Ireland
[c] Department of Materials Science and Technology, University of Crete, P.O. Box 2208, 71003 Heraklion, Crete, Greece
[d] Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas, P.O. Box 1385, 71110 Heraklion, Crete, Greece
[e] Catalan Institute for Research and Advanced Studies ICREA, 08010 Barcelona, Spain

ARTICLE INFO

Article history:
Received 14 September 2009
Received in revised form 3 December 2009
Accepted 9 December 2009
Available online 16 December 2009

Keywords:
Nanoimprint lithography
Dye-doped polymer
Light extraction
Plasmonic crystal
Photoluminescence

ABSTRACT

Photoluminescence of dye chromophores-loaded in printable polymer has been strongly enhanced thanks to two-dimensional nanoimprinted photonic crystals. Comparing the out of plane emission of the spin-coated dye-doped polymer on metallic corrugated and flat surfaces, the PL emission intensity increased by a factor 26 from the area with the nanostructure. This enhancement is explained by a coupling plasmon–exciton in the vicinity of the metal layer and an efficient diffraction of the surface plasmon modes by the metallic structures.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Improving the luminous efficiency, reducing the production cost, increasing the lifetime of OLEDs are the current key issues to be solved in order to achieve widely commercialized OLEDs. Only a small fraction of the total photons generated inside the film are generally usable, because of the total internal reflection and waveguiding effects of high-index layers. One solution to solve the light-trapping problem consists of using two-dimensional (2D) photonic crystals (PhCs) [1,2]. Nanoimprint lithography (NIL) can be used to transfer patterns of photonic crystal structures with high resolution (up to sub-10 nm) and excellent fidelity onto a very large number of organic compounds [3]. A second approach consists to increase the spontaneous recombination rate of the emitters by energy transfer between light emitters and surface plasmons (SPs). Several work on enhanced light emission via SPs have been described [4,5]. It has been shown that semiconductor light sources can be enhanced efficiently by surface plasmon in thin metal layers [6–8]. Studies have been recently, performed with dye-doped organic films [9–11] and with conjugated polymer films [12,13] in close proximity to metal surfaces. An important enhancement in the spontaneous emission intensity of emitters of dyes has been achieved by coupling its emission to surface plasmons generated by metallic thin film. The inherent surface roughness of an evaporated film was used for example to recover partially the energy trapped in SPP modes in the vicinity of a metallic surface [9,14]. In order to furthermore increase the photoluminescence intensity of the dye-doped polymer film, we investigated here the exciton-field coupling of nanoimprinted plasmonic crystals with dye chromophores-loaded.

2. Experiments

To realize nanoimprinted plasmonic crystals, silicon stamps with grating structures were produced by conventional UV lithography. Silicon is etched to a depth of 300 nm and treated with an anti-adhesive layer (tridecafluor-1,1,2,2-tetrahydrooctyl trichlorosilane) deposited in vapour phase resulting in a very low surface energy. The stamp is positioned inside a Petri dish on a hot plate at 250 °C (well above the tridecafluor-1,1,2,2-tetrahydrooctyl trichlorosilane boiling point). One drop of the anti-adhesive solution is placed in the Petri dish with a microsyringe and left there for 2 h. This treatment is very important in order to avoid sticking of the polymer to the stamp during the imprinting process and to facilitate demolding.

A 2.5 in. *Obducat* nanoimprinting tool was used to perform the imprints. A 300 nm film of mr-NIL 6000 (from *micro resist technology GmbH*) was spin-coated onto the glass wafer followed by soft baking at 100 °C for 5 min to evaporate the residual solvent. Stamp and polymer were brought into contact at a temperature of 90 °C

* Corresponding author. Address: Catalan Institute of Nanotechnology, Campus de Bellaterra, Edifici CM7, 08193 Barcelona, ES, Spain. Fax: +34 935868313.
E-mail address: vincent.reboud@cin2.es (V. Reboud).

0167-9317/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2009.12.030

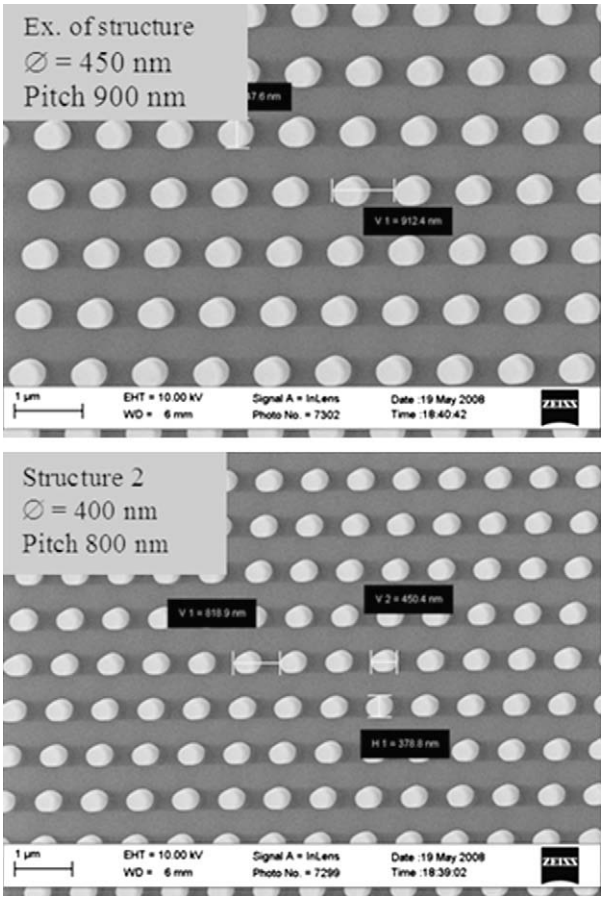

Fig. 1. SEM images of nanoimprinted metallic structures with their associated critical dimension.

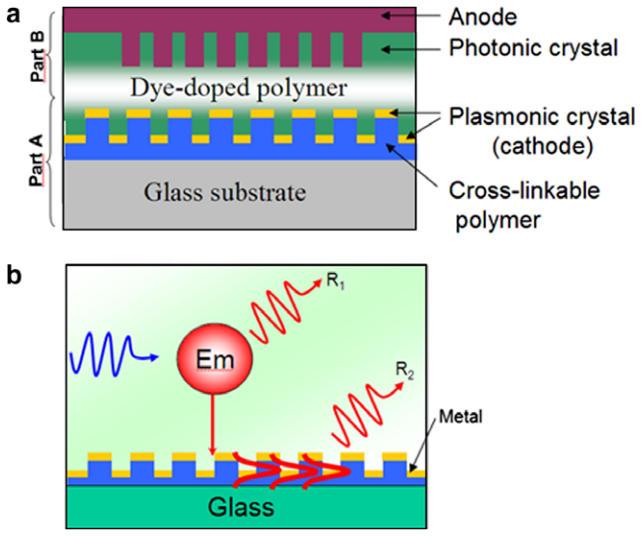

Fig. 2. (a) Cross-section schematic of the system. Part A shows the studied system in this manuscript. Part B presents the next fabrication step for potential OLEDs application and (b) schematic of the alternative recombination path (named R_2) to the conventional radiative recombination (named R_1) in the near field of the metal layer in order to enhance light extraction.

and a pressure of 60 bars for 5 min was applied. The separation of the stamp and the substrate was performed at 40 °C. The polymer was then UV cross-linked during 30 s followed by the evaporation of 50 nm Au thin film deposited on top cured nanoimprinted polymer layer (Fig. 1).

To prepare the photoluminescent polymer, rhodamine 6G (from Sigma Aldrich) was diluted in 1 mL of mr-NIL 6000 with a concentration of dye molecules of 5×10^{-4} M. The peak emission of R6G in the polymer was measured at 550 nm. A 300 nm film of the functionalized polymer was spin-coated onto the nanoimprinted metallic structures followed by soft baking at 60 °C for 5 min to evaporate the residual solvent. The overall stamp size used in our experiments is a $2 \times 2\ cm^2$ silicon stamp, including $2.5 \times 2.5\ mm^2$ patterned grating areas. Fig. 2a presents the cross-section schematic of the studied system composed by Part A – glass substrate, nanoimprinted polymer, thin evaporated metallic layer and spin-coated dye-doped polymer. Part B describes the eventual next fabrication step to achieve OLEDs configuration.

3. Results and discussion

To analyze the enhancement of light extraction, CDD images have been recorded through an epifluorescence microscope (excitation between 390 and 420 nm, emission collection from 450 nm). Four imprinted structures numbered from 1 to 4 have been tested with a pitch of respectively 700 nm (structure 1), 800 nm (structure 2), 900 nm (structure 3) and 1 μm (structure 4) and an associated half-pitch of respectively 350 nm (1), 400 nm (2), 450 nm (3) and 500 nm (4) (Fig. 3a). SEM images of two of structures are shown in Fig. 1. Fig. 3b shows the photoluminescence intensity of the four structures. High intensities are detected for the structures with the pitch of 800 and 900 nm (Fig. 1). The CCD camera presents a gain factor of 2.2. Fig. 3b has been plotted by taking in account the gain of the camera. Samples were then excited with the 514.5 nm line of an Argon laser with a power of 5 μW, the incident beam is normal to the surface. The PL is collected through a ×20 microscope objective and dispersed in a spectrometer with 0.1 nm spectral resolution. The PL data is recorded at room temperature. An emission spectra comparison of the unpatterned dye-doped polymer on a quartz substrate without metal, on quartz substrates coated with the nanoimprinted plasmonic crystals, is presented in Fig. 3c. A 4.5-fold enhancement in the PL peak intensity is observed for the unpatterned Au layer in comparison of the unpatterned dye-doped polymer on a quartz substrate without metal.

The transmission of the 50 nm Au layer spin-coated with undoped mr-NIL 6000 film was measured to a value of 18% at 550 nm. The metallic layer acts as a mirror by doubling the path of the pump and reflecting the emitted light. If the Au layer was acting as a pure mirror, a 3.28 enhancement in the PL peak intensity should be expected. The higher enhancement (×4.5) has been associated to the surface plasmon generated by the metallic layer suggesting a coupling with surface plasmons which are diffracted by the roughness of the metallic layer [9]. In the case of nanostructured metallic layers, an enhancement of a factor 26.1 has been measured for the nanoimprinted plasmonic crystal with a pitch of 900 nm compared to the dye-doped polymer film without metallic layer. A proposed explanation is the following. Excited electrons in the dye molecules couple to the free charges at the metal surface. The corrugation of the metallic film is used to recover partially the energy trapped in surface plasmon modes in the vicinity of a metallic surface as shown by the schematic of Fig. 2b. The nanostructured layers diffract differently the emitted light and the surface plasmon out of the plane. This new path of recombination (R_2 in Fig. 2b) is an extremely fast process [14]. The radiative lifetime of emitters is expected to decrease, due to the surface plasmon induced increase of density of electromagnetic modes in the neighbourhood of the emitters; thus higher number of photons are emitted leading to an increase in the PL intensity.

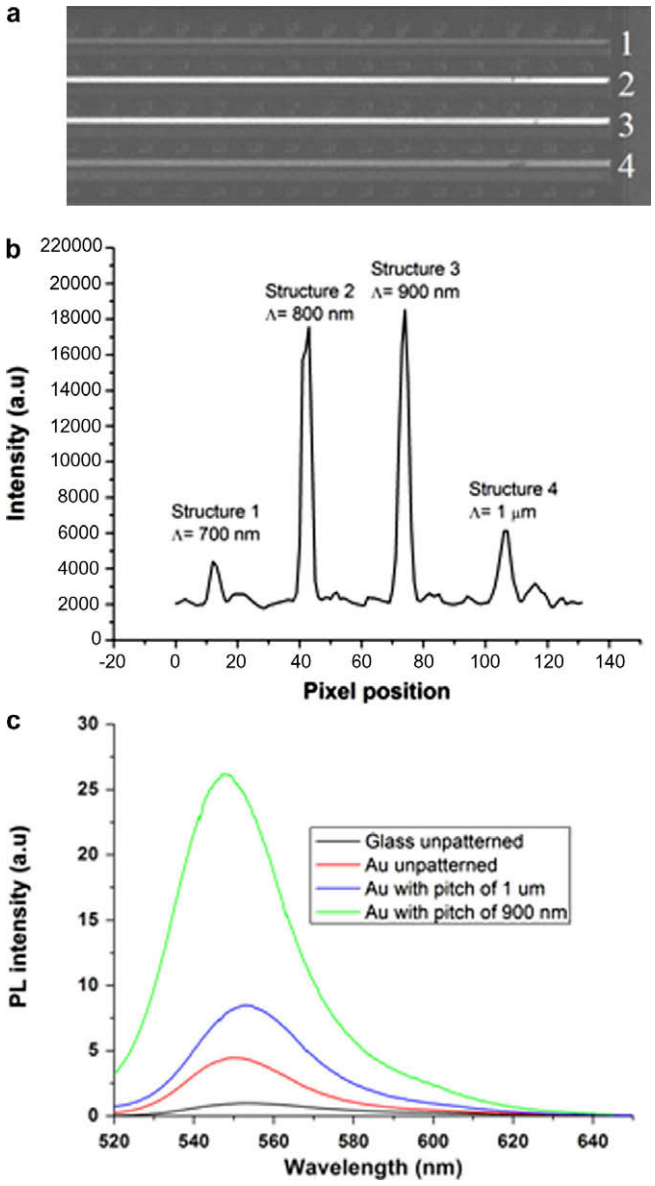

Fig. 3. (a) CDD image of imprinted structures through an epifluorescence microscope, excitation between 390 and 420 nm, emission collection from 450 nm. Structures 1–4 present, respectively a pitch of 700, 800, 900 nm, 1 μm. (b) Intensity of the four structures, and (c) photoluminescence spectra of a dye-doped polymer film on a quartz substrate (black line), on a unpatterned 50 nm Au quartz substrate (red line), on a patterned (pitch of 1 μm) 50 nm Au quartz substrate (blue line), on a patterned (pitch of 900 nm) 50 nm quartz substrate (red line). (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

To corroborate this explanation, a 200 nm layer of PMMA was spun between the corrugated Au layers and the dye-doped polymer layer. The PL enhancement was dramatically reduced; the surface plasmon penetration depth does not interact anymore in the active layer. The combination of surface plasmons and nanoimprinted structures in an active layer can lead to a new class of cost effective and high-efficiency OLEDs by using the metallic surface as an electrical contact as shown in Fig. 2a (Part A and B).

4. Conclusion

We explored the direct coupling of the light emitted by a dye-doped polymer to the surface plasmon modes at the periodic metal layer interfaces. A strong enhancement of the photoluminescence intensity has been achieved by controlling the geometry of the plasmonic crystals to recover the trapped energy in surface plasmon modes and to allow a greater enhancement of the component efficiency. We showed that nanoimprint lithography is a suitable and simple process to fabricate these plasmonic structures with no need to etch the residual layer. Our results show that the nanoimprinted plasmonic crystal slab structures are a potential candidate for high-efficiency OLEDs.

Acknowledgements

We grateful acknowledge Mads Brøkner Christiansen and Anders Kristensen to provide us the dye-doped polymer and Marc Zelsmann for his help in stamp fabrication. The support of the EC-funded project NaPANIL (Contract No. NMP2-LA-2008-214249) and the network of excellence Phoremost are gratefully acknowledged.

References

[1] Y.-J. Lee, S.-H. Kim, J. Huh, G.-H. Kim, Y.-H. Lee, S.-H. Cho, Y.C. Kim, Y.R. Do, Appl. Phys. Lett. 82 (2003) 3779.
[2] V. Reboud, P. Lovera, N. Kehagias, M. Zelsmann, C. Schuster, F. Reuther, G. Gruetzner, G. Redmond, C.M. Sotomayor Torres, Appl. Phys. Lett. 91 (2007) 151101.
[3] S.Y. Chou, P.R. Krauss, P.J. Renstrom, Science 272 (1996) 85.
[4] A. Köck, E. Gornik, M. Hauser, W. Beinstingl, Appl. Phys. Lett. 57 (1990) 2327–2329.
[5] W.L. Barnes, J. Lightwave Technol. 17 (1999) 2170–2182.
[6] J. Vuckovic, M. Loncar, A. Scherer, IEEE J. Quant. Electron. 36 (2000) 1131–1144.
[7] A. Neogi, C.-W. Lee, H.O. Everitt, T. Kuroda, A. Tackeuchi, E. Yablonvitch, Phys. Rev. B 66 (2002) 153305.
[8] I. Gontijo, M. Borodisky, E. Yablonvitch, S. Keller, U.K. Mishra, S.P. DenBaars, Phys. Rev. B 60 (1999) 11564–11567.
[9] V. Reboud, N. Kehagias, M. Zelsmann, M. Fink, F. Reuther, G. Gruetzner, C.M. Sotomayor Torres, Opt. Express 15 (12) (2007) 7190.
[10] T.D. Neal, K. Okamoto, A. Scherer, Opt. Express 13 (14) (2005) 5522.
[11] V. Reboud, N. Kehagias, M. Striccoli, T. Placido, A. Panniello, M.L. Curri, M. Zelsmann, F. Reuther, G. Gruetzner, C.M. Sotomayor Torres, J. Vac. Sci. Technol. B 25 (2007) 2642.
[12] T.D. Neal, K. Okamoto, A. Scherer, M.S. Liu, A.K.-Y. Jen, Appl. Phys. Lett. 89 (2006) 221106.
[13] P.A. Hobson, S. Wedge, J.A.E. Wasey, I. Sage, W.L. Barnes, Adv. Mater. 14 (2002) 1393–1396.
[14] K. Okamoto, I. Niki, A. Shvartser, Y. Narukawa, T. Mukai, A. Scherer, Nat. Mater. 3 (2004) 601–605.