9th Int. Symp. "Nanostructures: Physics and Technology"
St Petersburg, Russia, June 18–22, 2001

Comparison of dye photoluminescence spectra in direct and inverted opaline films

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Abstract. Changes introduced by a photonic bandgap environment in an emission spectrum of a light source have been compared for direct and inverted opals and a qualitative difference has been revealed.

Introduction

3-dimensional light emitting photonic bandgap (PBG) structures are periodical spatial ensembles of scatterers integrated with light sources, moreover the emission band of the latter has to be tuned with the PBG frequency range in order to realise the emission-to-structure feedback. Studied so far 3-dimensional photonic crystal light sources for the visible are based on opals. The closest approach to the complete PBG has been achieved with TiO_2 (refractive index (RI) contrast up to 2.7 to 1) [ ] and SnS_2 (RI contrast up to 3.4 to 1) inverted opals [ ]. These structures are incomplete due to an insufficient volume fraction of the dielectric, which is 10–13 vol.% instead of ~30% necessary for maximising the gap. Nevertheless, the scattering strength of these opaline structures is high enough to provide the strong interaction between the emitter and the emitted photon and thus to alter parameters of the spontaneous emission. In what follows we discuss the qualitative difference between emission spectra of organic dyes embedded in direct opal and in its SnS_2 replica.

1. Experimental details

Opaline films have been used in this work as those advance structurally over bulky opals [ ]. PMMA opaline films were formed from beads possessing a small amount of fluorescent dye (Coumarin 6) [ ] by casting the bead suspension on hydrophilized microscope slides. These thin film polymeric crystals consist of ca. 30–50 monolayers and possess domains extending over 100 s of micrometers. Dye molecules are distributed homogeneously in beads. The RI contrast as 1.5 to 1 and the filling fraction of 74% are characteristics of this photonic crystal. These films were used as templates to prepare inverted opals by synthesising SnS_2 in interstitials and subsequent dissolving of PMMA beads. As a light source the Perylene dye deposited on the inner surface of the inverted opal was used. The effective RI contrast in studied samples was about 2.1 to 1 and the SnS_2 filling fraction was about 13%. The plain Coumarin-loaded PMMA film and the unstructured SnS_2 film with Perylene coating, both on glass substrates, have been prepared as reference samples.

Photoluminescence (PL) spectra of Coumarin/PMMA opaline films have been collected within the ~5° fraction of the solid angle along the direction of the stop-band appearance.

The emission intensity of Coumarin in the opal is suppressed in the stop-band frequency range as compared with the reference sample (Fig. 1(a)). To demonstrate the relative changes in the number of photonic states in the PBG region, PL spectra are shown normalised to the PL spectrum on unstructured Coumarin-PMMA film (Fig. 1(c)). Stop-bands obtained from the emission are compared with transmission spectra of the PMMA opaline film (Fig. 1(b)). The stop-band related minimum appears at the same frequency and shows the similar depth in both transmission and emission spectra, moreover, the similarity of their angular dispersions is obvious.

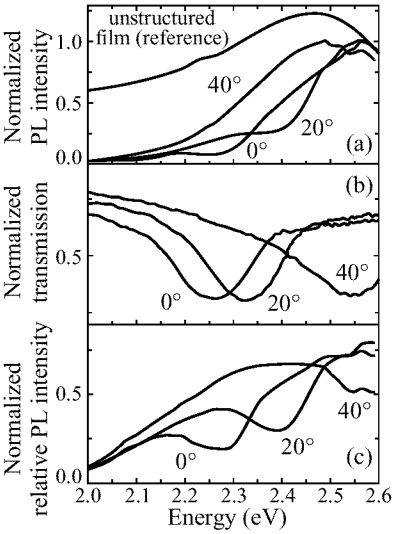

Fig. 1. Angle resolved PL spectra (panel a), transmission spectra (b) and relative PL spectra (c) of Coumarun/PMMA opaline film for angles of 0, 20, and 40 degrees. The reference PL spectrum is shown in the top panel.

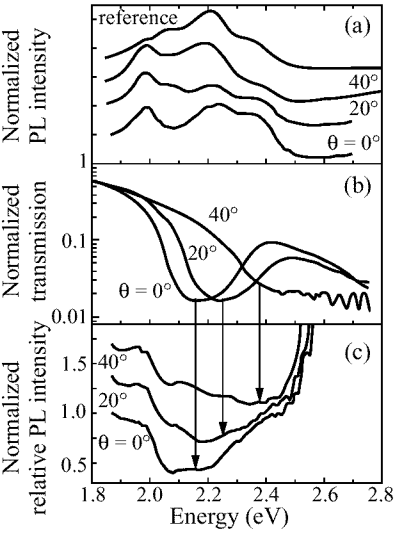

Fig. 2. The same as Fig. 1 for the Perylene/SnS_2 inverted opaline film.

PL spectra of SnS_2 inverted opal (Fig. 2(a)) have been measured under similar conditions as PMMA opals. Comparing them with the PL spectrum of the reference sample one can see the additional 1.98 eV band. Stop-band spectra extracted from the PL of Perylene in SnS_2 inverted opal (Fig. 2(c)) show a factor of 10 shallower minimum as compared with the stop-band in transmission (Fig. 2(b)). The stop-band angular dispersions are shown for both relative PL and transmission spectra.

2. Discussion

The crucial question to be addressed with regard to a PBG light source is physical mechanisms responsible for changes in the emission as compared with the free space case. To illustrate the role of the PBG incompleteness, the reconstruction of the PL spectra has been made by multiplying the PL spectrum of the reference sample with the transmission spectra of opaline films measured at certain angles. In the case of PMMA opal the reconstructed PL spectra (Fig. 3) correlate well with those observed for specified angles. As well, fitting of the reconstructed PL spectrum with the observed one for the Perylene/SnS_2 opaline film can be achieved under certain circumstances for angles close to [111] direction. However,

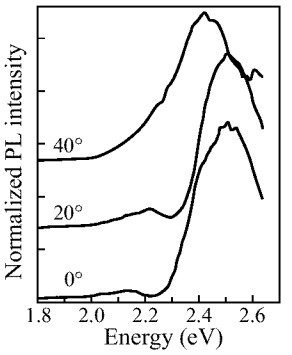

Fig. 3. Reconstructed PL spectra of Coumarun/PMMA opaline film for angles of 0, 20, and 40 degrees.

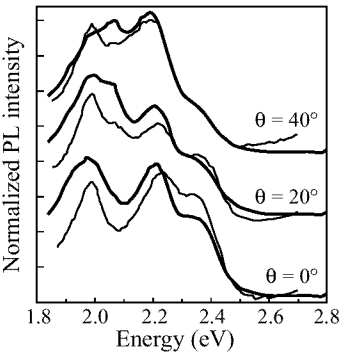

Fig. 4. The same as Fig. 3 for the Perylene/SnS_2 inverted opaline film. Bold and thin lines represent reconstructed and experimental spectra, respectively.

with further deviation from this direction the reconstructed spectra do not reproduce the 1.98 eV emission band (Fig. 4).

There are two scenarios can be followed. The first one is realised in the PMMA opaline film, whose PBG does not affect the spontaneous emission but simply changes the angular distribution of the emission flow in accord with the transmission function. The angular dispersion of this band-pass filtering relates to the incompleteness of the PBG. Certainly, with the broadening of the stop-band and squeezing of its dispersion occurring in SnS_2 inverted opaline films, a more intimate relation between the emission and the PBG structure can be expected. The physical reason is the development of the dip in the density of the photon state profile, which is an integral of state numbers over the whole solid angle (see e.g. [5]). The corresponding spectral redistribution of the emission flow acquires the angular independence, to which feature the angular independent 1.98 eV PL band is tentatively ascribed.

In summary, we have studied the emission of organic dyes from direct and inverted opaline films. The suppression of the emission intensity in direct opals can be referred as its angular redistribution due to the decrease of the number of photon states in a given direction. The enhancement of the PBG in inverted opals results in the co-existence of effects related to both the density and the number of photon states, which appears as the persistent spectral redistribution of the emission out of the PBG frequency range as well as the angular redistribution of the emission flow.

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