Optical Probes inside Photonic Crystals

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Introduction

The spontaneous emission of an atom is not a property of the atom only; it also depends on the local optical surroundings.[1] The simplest demonstration of this effect was provided by the early experiments of Drexhage, who studied the emission rate of luminescent europium ions close to a mirror.[2] It was found that while the spectral distribution of the emission remained constant, the emission rate was dependent on the position of the Eu^{3+} ions relative to the mirror. This effect is due to interference of the optical modes incident to and reflected at the mirror. Since then, the modified spontaneous emission of atoms in cavities has been studied extensively.[3] More recently, the control of spontaneous emission in solid-state systems has become of great interest because it enables the tailoring of the emission properties of optical materials. It was shown how the spontaneous-emission rate of optical probe ions or dyes inside dielectric films is modified by the presence of a dielectric interface,[4,5] in a dielectric multilayer,[6,7] or a microcavity.[8,9] The dependence of the decay rate on the optical surroundings in these one-dimensional systems can be described in terms of Fermi's "golden rule," which states that the decay rate is proportional to the local optical density of states (DOS). The spatial variation in the DOS is due to the interference of optical modes reflected and refracted at the dielectric interface(s).

Photonic crystals are predicted to have a radical effect on the spontaneous-emission rate.[10,11] In crystals with a full bandgap, spontaneous emission at frequencies inside the gap will be fully suppressed because the optical modes do not exist (DOS = 0). Photonic crystals with a partial gap can also have a significant effect on the spontaneous-emission rate, and large spatial variations in the local DOS are predicted in some cases.[12–14] While great progress has been made in past years in the fabrication of a large variety of photonic-crystal structures, measurements of the spontaneous-emission rate are still scarce. In this article, we present recent work in Amsterdam on the modified emission of optical probes incorporated inside photonic crystals and make reference to work by other authors in this area. Applications of controlled spontaneous emission in photonic-crystal lasers are also reviewed.

Optical Probes inside Colloidal Photonic Crystals

A large variety of colloidal photonic crystals have been fabricated to date (see the article by Colvin in this issue). If optical probes are incorporated inside the colloids, the effect of band structure on the spontaneous emission can be studied. So far, two classes of light sources have been used: dyes and lanthanide ions. A dye is an organic complex with a luminescent ligand; a large variety of different dyes, with emission spectra varying over the full visible spectral range, are available. Dye processing is compatible with the typical wet-chemical processing routes used in colloid fabrication. More recently, lanthanide ions such as europium, terbium, and erbium are also being considered as optical probes in colloids. They can be incorporated by ion implantation[15] or wet-chemical processing.[16] Optical transitions in these ions occur in the 4*f* electronic shell that is shielded from the surroundings by two closed outer 5*s* and 5*p* shells. Hence, the emission from these ions is relatively insensitive to the host, and high luminescence quantum efficiencies can be achieved. Lanthanide ions have sharp emission spectra, with wavelengths extending from the visible to the near-infrared (1.5 μm), depending on the ion.

Figure 1a shows photoluminescence decay traces of Er^{3+} ions that have been incorporated into spherical SiO_2 colloids with a diameter of 340 nm using Er^{3+} ion implantation. The ions are excited using a pulse from an Ar ion laser at 488 nm, and the emission at 1.54 μm is monitored as a function of time after the laser is switched off. A decay rate of 69 s^{-1} (corresponding to a $1/e$ lifetime of 14 ms) is observed. If the colloids are immersed in an index-matching fluid ($n = 1.45$), the decay rate increases to 101 s^{-1} (10 ms). The change in emission rate is fully reversible if the liquid is removed. This is the simplest demonstration of a photonic effect in a *single* microsphere and is a result of the change in the DOS due to the changing optical surroundings. Figure 1b shows the DOS inside a SiO_2 microsphere in air calculated as a function of diameter (horizontal axis) and normalized radial distance (vertical axis) indicated by a gray scale normalized to the DOS in bulk SiO_2. Several minima and maxima in the DOS are observed as a function of sphere diameter and can be related to so-called Mie resonances or normal modes of the microsphere. The calculation in Figure 1b clearly demonstrates the concept of local DOS; that is, the optical emission rate is a strong function of position inside the photonic structure. It also demonstrates that strong effects can be observed in a system as simple as a single microcavity.

Figure 2a shows the fluorescence spectrum of a rhodamine isothiocyanate dye incorporated in silica colloids (dashed line). A broad spectrum peaking at 580 nm is observed. Figure 2a also shows the fluorescence spectrum measured on a weakly interacting photonic crystal composed of rhodamine isothiocyanate dye-doped silica spheres suspended in water (solid line).[17,18] A clear dip in the spectrum is observed. The solid line in Figure 2b shows the ratio of the two spectra in Figure 2a, the "transfer function." It has been normalized to 100% at long wavelengths, where no photonic-crystal effects occur. It is apparent from Figure 2 that the photonic crystal changes the fluorescence spectrum of the dye considerably: the spectrum acquires a pronounced stop gap. The stop gap is caused by the fcc (111) crystal planes that are normal to the direction of observation. The crystal planes act as Bragg mirrors for the fluorescence, preventing part of the light from leaving the crystal. We observed that the central wavelength of the stop gap depends on the density of spheres in the crystal and also upon the direction of observation, in agreement with Bragg's law (taking into account an averaged refractive index).[19]

For comparison, in Figure 2b we have also plotted a transmission spectrum measured for plane waves entering the crystal from outside (dotted line). The stop gap in the transfer function has the same central wavelength of 580 nm as that in the conventional transmission spectrum; but the

stop gap in the transfer function is narrower. Furthermore, the maximum attenuation for internal sources is much less than that for external plane waves, which has also been observed by other groups.[20] From detailed experiments,[17] we conclude that scattering by defects, in particular near the surface of the sample, plays a key role. Light emitted in the direction of a stop gap is Bragg-attenuated, but light can propagate freely in other directions. This light can be scattered by a small concentration of imperfections that are inevitable in any real crystal. Radiation scattered by defects deep inside the crystal will experience attenuation similar to that observed in a plane-wave experiment. If light is scattered by defects close to the surface of the crystal, however, this radiation emerges from the crystal unattenuated. Thus, light appears in the direction of a stop gap. Apparently, the role of a crystal in modifying the emission spectra is richer than providing simple filter action.

The presence of a clear stop gap in the emission spectrum suggests that the photonic band structure may also affect the radiative lifetime. Therefore, a time-resolved emission study was undertaken of dye in colloidal photonic crystals.[18] Figure 3 shows two typical measurements of fluorescence intensity versus time. The lower trace is of dye in a colloidal photonic crystal, for a frequency inside a stop gap. The upper trace is for dye in colloidal liquid, which is considered a "nonphotonic" reference. The fluorescence decay is very close to a single exponential over nearly three decades, which indicates that unwanted interaction between dye molecules is absent.[21] The lifetimes for the curves are both 3.5 ns, that is, there is little difference in decay between the crystal and the reference. We have also studied lifetimes as a function of frequency for crystals with different densities. The variations in lifetime are of the order of only 0.05 ns, or 2%. Again, no significant photonic-crystal effect was observed. Thus, the influence of the photonic band structure on lifetime in these crystals is small, even though a large change in the spectra is observed (Figure 2a). These data are in good agreement with a simple

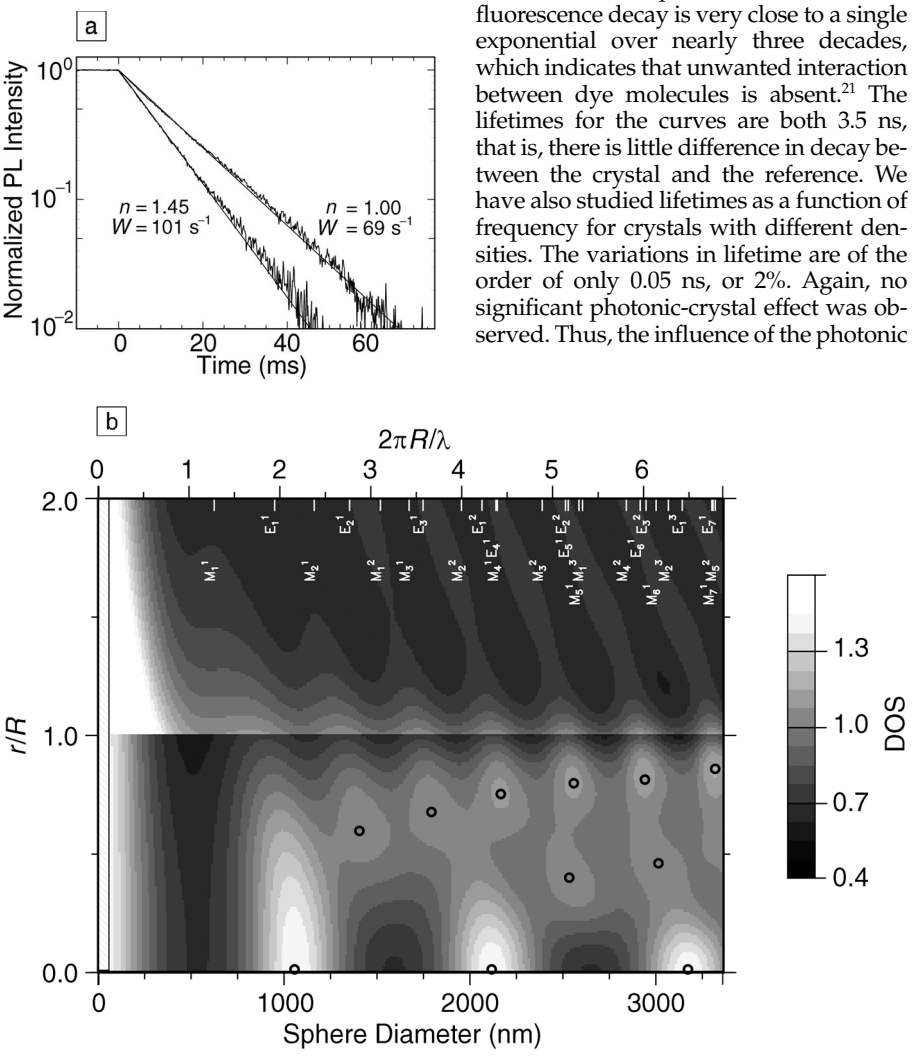

*Figure 1. (a) Photoluminescence (PL) decay measurements at 1.54 μm of Er-doped SiO_2 microcavities in air and in an index-matching fluid (*n = 1.45*).* W *is the decay rate. (b) Calculated density of states (DOS) (λ = 1.54 μm) in a spherical SiO_2 microcavity as a function of diameter (horizontal axis) and normalized radial distance (vertical axis);* r *is the distance from the sphere center and* R *is the sphere radius. The DOS is indicated by a gray scale (see bar on the right). (From Reference 7.)*

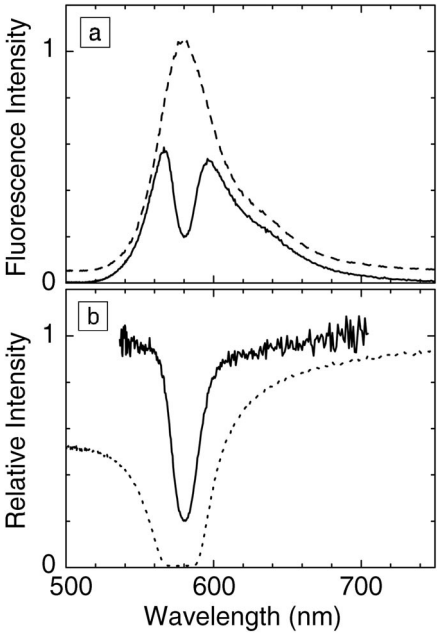

Figure 2. (a) Fluorescence spectra from rhodamine isothiocyanate dye-doped silica colloids in a disordered suspension (dashed line) and in an ordered photonic crystal (solid line). (b) Transfer function [ratio of the two spectra in (a), solid line] compared with a transmission spectrum measured for an external source (dotted line). All spectra were taken perpendicular to the fcc (111) crystal planes. (From Reference 17.)

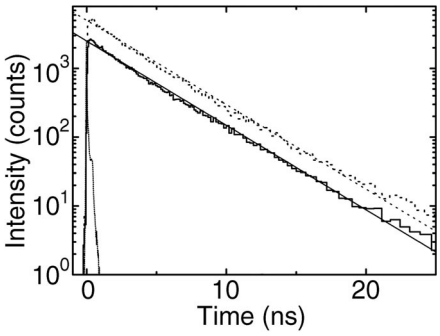

Figure 3. Fluorescence decay of dye inside a colloidal photonic crystal of 65 vol% silica particles in water (solid curve) and in a colloidal liquid (dotted curve, offset by a factor of 2), at λ = 577 nm. The drawn and dotted lines represent decay curves with mean lifetimes of 3.54 ± 0.02 ns. (From Reference 18.)

model inspired by studies of atoms in Fabry–Pérot cavities,[3] in which the relative change in radiative lifetime is assumed to be equal to the total solid angle subtended by the Bragg reflections divided by a 4π solid angle. An advanced theoretical description has recently been made, wherein the DOS was calculated numerically.[22] For silica or polystyrene colloidal crystals and opals, a change in emission rate of less than 5% was found, in good agreement with the data of Figure 3. Apparently, a large change in the fluorescence spectrum can coincide with a minor change in fluorescence lifetime.

To observe large modifications of spontaneous-emission rates and even full suppression of spontaneous emission, light sources must be placed in a photonic crystal that strongly interacts with light. One way to produce such crystals is through self-organization, resulting in inverse opals or air-sphere crystals in materials with high refractive indices (see the article by Colvin in this issue). We have measured angle-resolved emission spectra from a laser dye (Nile blue) infiltrated in a titania inverse opal.[23] Figure 4a shows spectra for various detection angles α from the normal to the (111) surface plane.[24] At $\alpha = 0°$, the emission is greatly suppressed over a wide frequency range by the first-order stop gap. The bandwidth of the stop band is comparable to the broad spectral range of the dye; hence, the spectrum is significantly altered. The large relative bandwidth of 15% is a signature of a well-ordered photonic crystal that strongly interacts with the light. It is apparent from Figure 4 that with increasing α, the frequency range of suppressed emission moves toward high frequencies, as expected for simple Bragg diffraction. For emission in excess of $\alpha = 60°$, the stop band no longer overlaps the emission spectrum.

To obtain directional emission properties, the emission spectra are divided by spectra that are not modified by Bragg diffraction (see Figure 4b). At $\alpha = 0°$, the stop gap is readily apparent, and the emission is attenuated by 75% near the center of the gap. The attenuation is limited by a mechanism akin to the one described earlier, in agreement with the estimate $(1–l_B/l)$, where l_B is the Bragg attenuation length and l is the mean free path for diffusion. At low α, single, broad stop bands are revealed in Figure 4b. Interestingly, at higher angles there appears to be a transition to a *double* stop band. The lower-frequency stop bands are denoted by S_1, and the higher-frequency ones by S_2. With increasing α, the S_2 stop band becomes more apparent, while S_1 decreases in amplitude. Further analysis reveals that the frequencies of the S_1 and S_2 stop-band edges show a so-called avoided crossing as a function of α, which is the result of multiple Bragg diffractions: the (200) Bloch mode mixes with the (000) and (111) modes. The emission data agree well with reflectivity data and with stop gaps calculated by the plane-wave expansion method.[26]

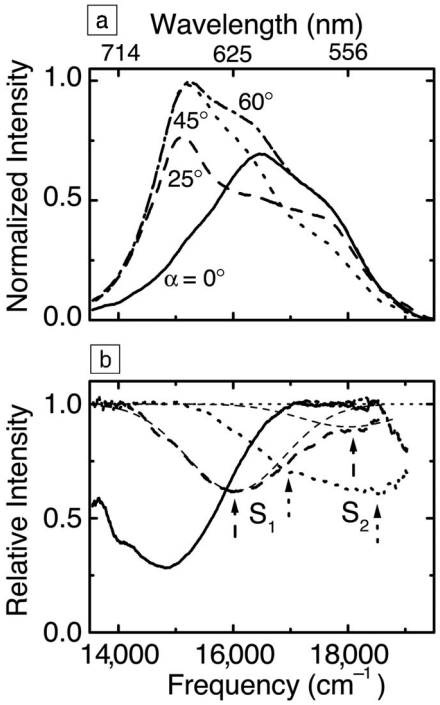

Figure 4. (a) Normalized emission spectra as a function of frequency for Nile blue dye in titania inverse opal. (b) Relative intensities, obtained from the spectra in (a). Solid curves are for $\alpha = 0°$, dashed curves for $\alpha = 25°$, dotted curves for $\alpha = 45°$, and dash-dotted curves for $\alpha = 60°$. The S_1 and S_2 stop bands in (b) at $\alpha = 25°$ are indicated by thin dashed lines, and the centers of these stop bands are indicated with arrows (dashed for $\alpha = 25°$, dotted for $\alpha = 45°$). (From Reference 24.)

Optical Probes in Photonic Crystals Made Using Lithography

The titania-based inverted opal structure described in the last section shows strong interaction with light, but probably does not possess a full bandgap. We have studied the photoluminescence from Si-based three-dimensional photonic crystals based on the "woodpile" structure made by Lin et al.,[27] which do possess a full bandgap. A scanning electron microscopy (SEM) image of the structure is shown in the inset of Figure 5. It was found that the polycrystalline silicon used in the fabrication shows a broad emission spectrum in the near-infrared when optically pumped at $\lambda = 488$ nm (see solid curve in Figure 5).[28] The luminescence is attributed to optical transitions at defects or grain boundaries in the Si. In this way, the photonic crystal itself acts as a light source, which makes it ideal for studies of the modification of spontaneous emission in these structures. Figure 5 (dashed curve) also shows the luminescence spectrum measured on a photonic crystal composed of five layers of Si "logs" (i.e., 1.25 unit cells). Clearly, the emission is suppressed over a broad spectral range, consistent with the calculated bandgap region (indicated on top of the figure). To study the effect on spontaneous emission of Er^{3+} probe ions, Er^{3+} was implanted in both the reference layer and the photonic crystal. The Er^{3+} peak at 1.54 μm is clearly observed in Figure 5 and is reduced in the photonic crystal. More measurements are required to further identify the influence of edge effects and the local DOS on the changes in spontaneous emission.

While two-dimensional photonic crystals do not possess confinement in the third dimension, they have two great advantages: they can be integrated with standard two-dimensional integrated-optics technology, and external probes (incident from the third dimension) can be used to probe their local DOS. Calculations show that strong modifications in the local optical DOS can be attained in these structures.[13,29] We have fabricated two-dimensional photonic crystals based on a cubic array of Si pillars using electron cyclotron resonance-etching techniques (see Figure 4 in the introductory article in this issue).[30] Next, we have developed two different wet-chemical processes to coat the Si photonic crystals with optical probe ions. In a first approach, Si pillars were coated with a thin SiO_2 film doped with an eosin dye. A modified base-catalyzed sol-gel process based on the decomposition of tetra-ethoxysilane was used, leading to the growth of a 45-nm-thick dye-doped oxide film on the pillars. The inset in Figure 6 shows a cross-sectional image of the photonic crystal, made using a fluorescence confocal optical microscope.[31] It can be seen that the full surface of the structure is coated with the fluorescent layer. Next, we developed a method to coat a photonic crystal with luminescent Er^{3+} ions.[32] The crystal is dipped in an $ErCl_3$ solution and subsequently oxidized and annealed. Figure 6 shows photoluminescence spectra of Si pillar structures with a relatively large pitch (4 μm, 8 μm, and 16 μm). The luminescence intensity increases with decreasing pitch due to the larger surface area

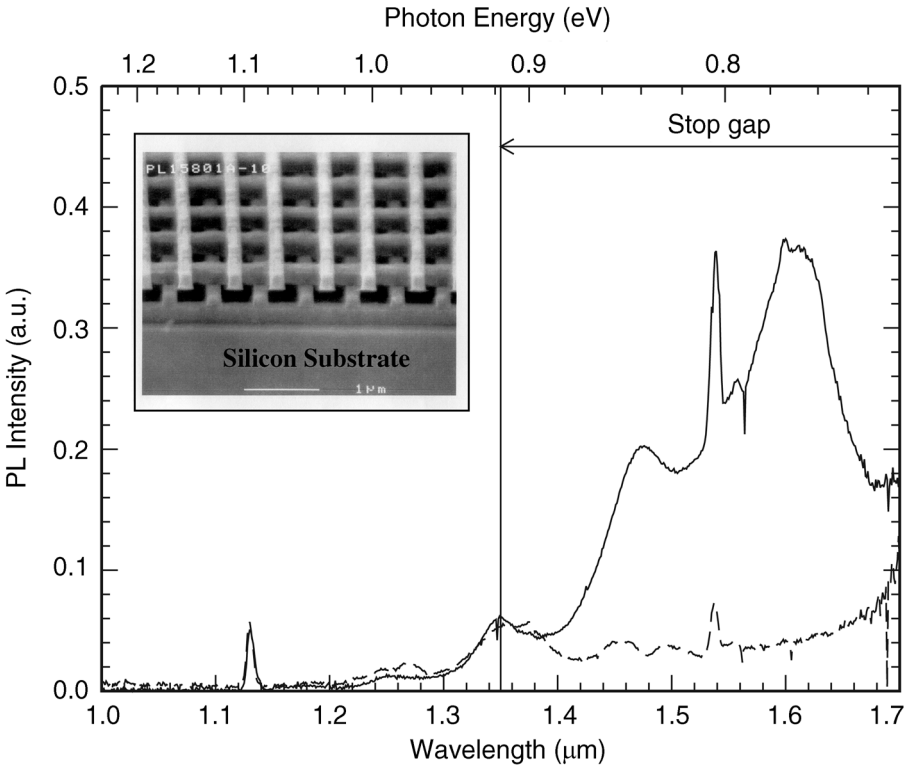

Figure 5. PL spectra of Er-implanted polycrystalline Si thin film (solid line) and three-dimensional photonic crystal (dashed line), based on Si "woodpile" structure, both measured at 15 K. $\lambda_{pump} = 488$ nm. The calculated stop-gap region is indicated on top. The inset shows a scanning electron micrograph of the structure. (From References 27 and 28.)

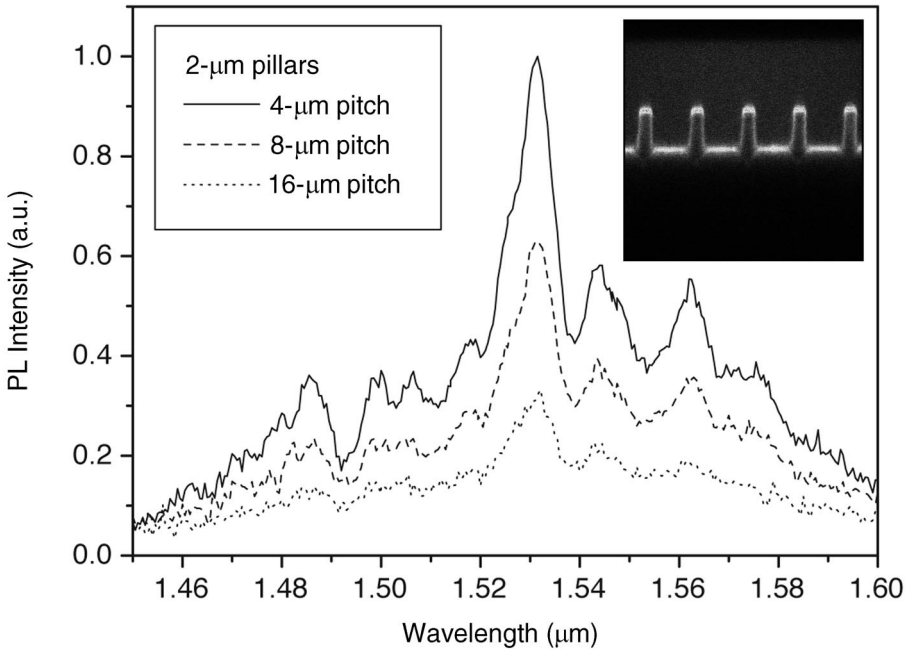

Figure 6. Luminescence spectra of a two-dimensional Si photonic crystal coated with an Er-doped SiO_2 film using a wet-chemical technique ($\lambda_{pump} = 488$ nm). Data are shown for pitches of 4 μm, 8 μm, and 16 μm. The inset shows a cross-sectional image of a Si photonic crystal coated with an eosin dye, imaged using confocal optical microscopy. (From Reference 31.)

excited in the laser spot. The next challenge is to measure the effect of the photonic band structure on the Er^{3+} emission at 1.53 μm from structures with smaller pitch that have a bandgap centered around 1.5 μm. The simplicity and flexibility of these novel coating techniques make them ideal for applying optical probes in a large variety of two- and three-dimensional photonic-crystal structures.

Photonic-Crystal Lasers

In this article, we have focused on the use of localized optical probes that are incorporated at well-defined positions in photonic crystals. In this way, changes in the spontaneous-emission rate can be related to the local optical DOS. Complete control over emission and channeling spontaneous emission into stimulated emission modes will be major achievements in the field. Several interesting experiments along these lines have already been reported. Vlasov et al. have infiltrated small CdS semiconductor particles into opals and observed optical gain that is enhanced by Bragg diffraction in the photonic crystals.[33] Stimulated emission has been studied in opals doped with high-gain organic media by Frolov et al.[34] At high excitation intensities, an intricate, finely structured spectrum is observed, reminiscent of random laser action that is mediated by multiple scattering in disordered photonic materials.[35] Painter et al.[36] and Boroditsky et al.[37] have fabricated two-dimensional photonic crystals in GaAs, in which the semiconductor host was used as a light source itself. A planar laser was made by this group, with the emission determined by a defect in the photonic crystal fabricated inside the active layer. Meier et al. have fabricated a polymer-based laser[38] with emission modified by a photonic crystal fabricated in the active layer. Here, by proper engineering of the geometry defects, light was efficiently coupled out in the direction perpendicular to the films.

Acknowledgments

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