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Defect-mode mirrorless lasing in dye-doped organic/inorganic hybrid one-dimensional photonic crystal

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We have developed a dye-doped organic/inorganic hybrid one-dimensional (1D) photonic crystal containing a dye-doped defect layer for defect-mode photonic band gap lasing. The multilayer laser structure consists of alternating layers of titania nanoparticles and polymethylmethacrylate (PMMA) with an active emission layer of organic dyes in PMMA. Low threshold lasing has been demonstrated at a single defect-mode wavelength of the 1D photonic band gap structure resulting from the inhibited density of states of photons within the stop band and the enhanced rates of spontaneous emission at the localized resonant defect mode. *© 2006 American Institute of Physics*.
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Periodic modulation of the dielectric constant forms a photonic band gap (PBG), the optical analog of electronic band gap in semiconductors.[1,2] Among many unique properties of photonic crystals, control of spontaneous emission by means of modification of the photon density of states has been of special interest since the performance of various optoelectronic devices such as lasers,[3] light emitting diodes,[4] or solar cells[5] is often limited by spontaneous emission. It has been shown theoretically[6,7] as well as experimentally[8,9] that when the transition frequency of the gain material confined in a photonic crystal is matched with the frequency range of the photonic band gap, the spontaneous emission is rigorously inhibited by the low density of states in the gap. As the depletion of the excited state by spontaneous emission is decreased, the spontaneous emission at the band edges or at defect modes purposefully introduced into the gap can be significantly enhanced and can produce a low-threshold or even thresholdless lasing. In this regard, there have been considerable efforts to fabricate photonic band gap laser devices either as a distributed feedback lasing[10,11] at band edge frequencies or as a defect-mode lasing[12,13] at localized defect-mode frequencies within the gap. In particular, due to the relative simplicity of fabrication, one-dimensional (1D) photonic crystal laser devices have been extensively studied.[12,14–18] For example, Kopp *et al.* demonstrated photonic band edge lasing from a 1D photonic crystal of dye-doped cholesteric liquid crystal.[14] More recently, Ozaki *et al.* showed electrically tunable defect-mode lasing in 1D photonic crystal of alternating TiO_2/SiO_2 multilayers using a conducting polymer as a gain medium and a nematic liquid crystal as an electrically tunable defect layer.[12]

In the present study, an organic/inorganic hybrid 1D photonic crystal with organic laser dyes as a gain medium is used to demonstrate a low threshold defect-mode lasing action. We employed inorganic titania (TiO_2) nanoparticles and polymethylmethacrylate (PMMA) as high and low index dielectric materials for constructing a distributed Bragg reflector having a 1D photonic band gap. TiO_2 nanoparticles were prepared following the synthetic scheme reported by Sanchez *et al.*[19] The nanocrystalline TiO_2 particles were composed of *anatase* phase (refractive index ~1.78 at 500 nm) with an average diameter of 4 nm as characterized by x-ray diffraction (Rigaku high resolution 250 mm diffractometer), spectroscopic ellipsometry (M2000, J. A. Woollam Co., Inc.) and transmission electron microscopy (JEOL 2000FX, 200 kV). Due to the organic surface capping group of acetylacetone, the TiO_2 particles were readily dissolved in a polar organic solvent such as butanol. The nanoparticles formed a thin film with excellent optical transparency, with a surface roughness in the order of a few nanometers. PMMA (Aldrich, M_W: 15 000 g/mole) was used as received and dissolved in toluene. As a defect layer containing a gain medium, the laser dye, 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (DCM) (Exciton), was dissolved in toluene at a concentration of 0.5 wt % with respect to PMMA. In order to fabricate the defect-mode 1D PBG laser structure, solutions of TiO_2 (in butanol), PMMA (in toluene), and DCM/PMMA (in toluene) were sequentially spin coated.

We designed the defect-mode laser structure based on photophysical properties of the gain medium. The linear ab-

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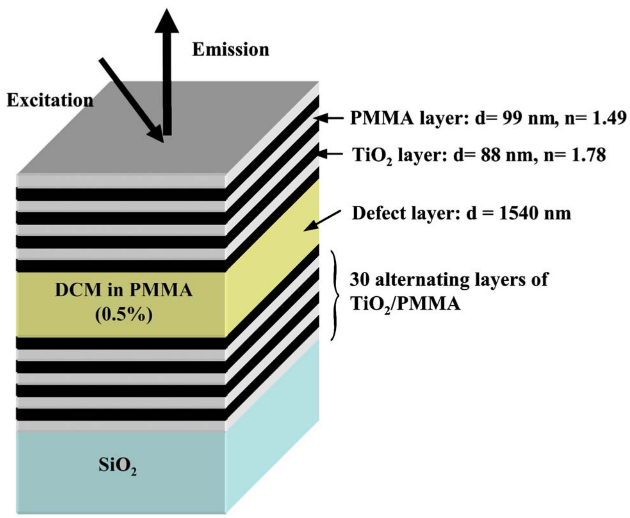

FIG. 1. (Color online) Schematic of dye-doped defect-mode 1-D photonic crystal, glass-$(PMMA\text{-}TiO_2)^{15}$-(DCM/PMMA)-$(TiO_2\text{-}PMMA)^{15}$-air.

sorption and emission spectra (excitation at 400 nm) of the thin film of DCM (0.5 wt %) in PMMA were obtained on a Hewlett-Packard 8453 diode array spectrophotometer and a SPEX Fluorolog-τ2 spectrofluorometer. The peak wavelength of absorption and emission is around 466 and 582 nm, respectively.

The defect-mode PBG structure, glass-$(PMMA\text{-}TiO_2)^{15}$-(DCM/PMMA)-$(TiO_2\text{-}PMMA)^{15}$-air, consists of 61 alternating layers of TiO_2, PMMA, and a central defect layer containing DCM in PMMA as schematically shown in Fig. 1. The average refractive indices of TiO_2, PMMA, and DCM in PMMA over the visible wavelength regime (400–700 nm) were measured by spectroscopic ellipsometry. The thicknesses of the corresponding layers were determined from the calculation of reflectance spectra using the transfer matrix method,[20] such that the peak wavelength of the gain medium emission was located at the wavelength of defect mode of the 1D photonic crystal in order to increase the lasing probability. The number of defect modes and their locations can be readily controlled by changing either thickness or refractive index of the defect layer. Figure 2(a) shows the calculated reflectance spectrum of the defect-mode 1D photonic crystal at normal incidence, in which the arrows indicate the defect modes inside the stop band. The high frequency defect mode is purposefully located at 582 nm, coincident with the peak wavelength of emission of the DCM dye in the PMMA. The inset in Fig. 2(a) is the corresponding density of states of photons, which is normalized with respect to the density of states in vacuum. The experimental reflectance spectrum in Fig. 2(b) was measured using an optical microscope (Zeiss Axioscop) equipped with a fiber-optic spectrometer (Stellarnet EPP2000) with a silver-coated metallic mirror as a 100% reference. Due to the numerical aperture of the objective lens [10×, numerical aperature (NA)=0.3], the spectrum in Fig. 2(b) is not a pure normal incidence reflectance but represents a convolution of multiple reflectance spectra over the incidence angles of 0° to ~17.5°.

The defect mode laser structure was optically pumped with frequency-doubled pulses of a *Q*-switched Nd:yttrium-aluminum-garnet laser (Continuum NY 61, λ=532 nm, pulse width=5 ns, repetition rate=50 Hz). The pump laser beam

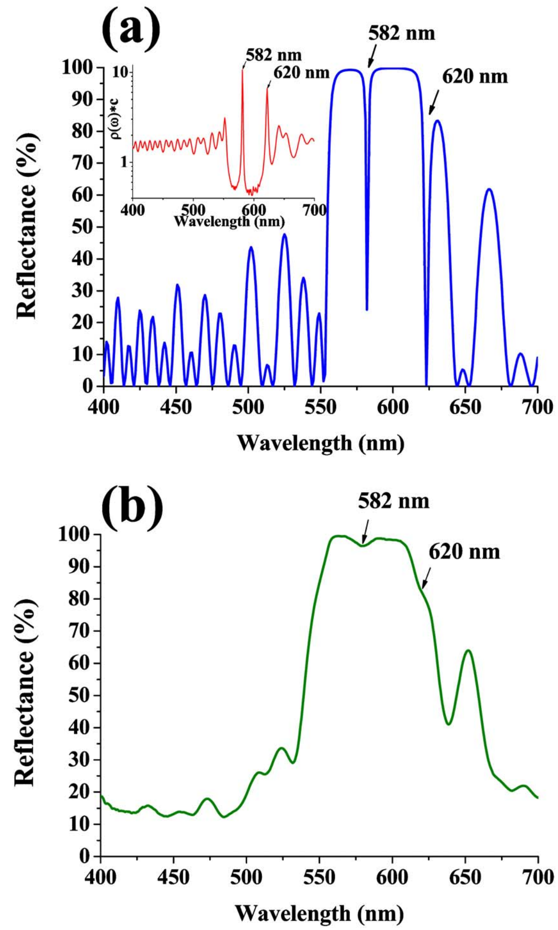

FIG. 2. (Color online) (a) Calculated reflectance spectrum of the defect-mode 1-D photonic crystal, glass-$(PMMA\text{-}TiO_2)^{15}$-(DCM/PMMA)-$(TiO_2\text{-}PMMA)^{15}$-air, at normal incidence of light by transfer matrix method. Arrows indicate the localized defect modes. The inset shows calculated density of states of photons, $\rho(\omega) \equiv dk/d\omega$, of the defect-mode 1-D photonic crystal, in which y-axis shows normalized $\rho(\omega)$ with respect to the value in vacuum $\rho(\omega)_{vac}=1/c$. (b) Measured reflectance spectrum of the fabricated defect-mode 1-D photonic crystal at near normal incidence using a reflection-mode optical microscope connected to a fiberoptic spectrometer.

was focused onto the sample with a lens of 20 cm focal length and 5 cm diameter with an incidence angle of 40° (from the normal), giving a beam diameter at the sample of about 300 μm. Lasing occurred in both the forward and backward directions and the backward emitted light was collected and focused onto a fiber-optic spectrometer (Ocean Optics USB 2000). The average power of the excitation pulses was controlled with a neutral density filter.

Figure 3(a) shows a photograph of the lasing beam on a white background, in which a highly directional emission parallel to the surface normal of the sample clearly indicates the lasing action as the pump power was increased above a lasing threshold. The corresponding emission spectrum is shown in Fig. 3(a), where strong single-mode lasing was observed at the expected defect-mode wavelength of 582 nm. The two small peaks beside the lasing line correspond to the excitation beam (532 nm) and the spontaneous emission at the lower frequency defect mode (~620 nm) below a lasing threshold. In order to confirm a lasing activity, the usual pump power dependence of the emission intensity at the lasing wavelength was obtained as shown in Fig. 3(b). In our experimental conditions, the lasing threshold was measured to be ~17 mJ/cm^2 (12 μJ/pulse on the area of

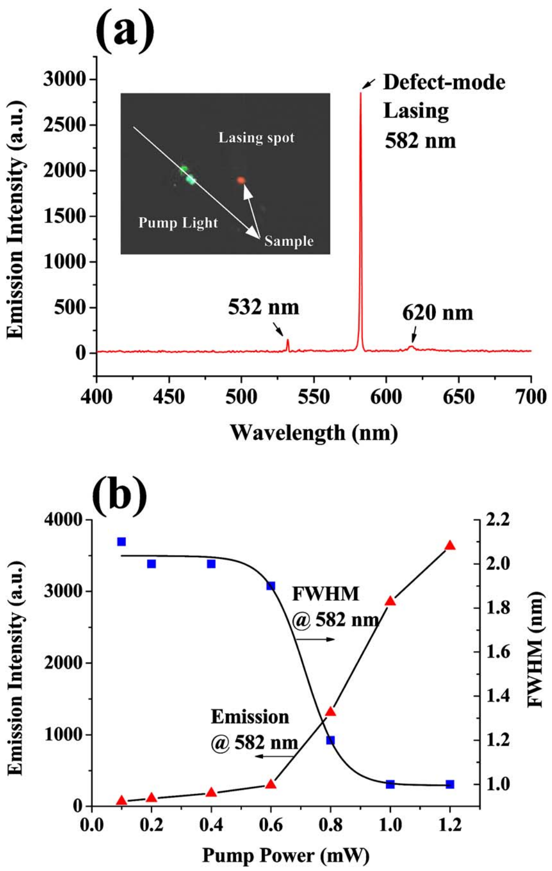

FIG. 3. (Color online) (a) The lasing spectrum obtained at a pump power of 1 mW, above the lasing threshold. The two small peaks beside the lasing line at 582 nm correspond to the excitation (532 nm) and low frequency defect mode (620 nm) below a lasing threshold. The inset shows a photograph of the 582 nm lasing from the defect-mode 1-D photonic crystal. A highly directional lasing action in backward direction was observed on a white background. (b) Emission intensity and linewidth (FWHM) at the lasing wavelength (582 nm) as a function of pump power, which clearly shows a threshold for lasing around 0.6 mW pump power (12 μJ pulse energy).

300 μm diameter). The spectral narrowing of the emission above the lasing threshold was also observed. The full width at half maximum (FWHM) of the emission line at the lasing wavelength decreased from 2.1 to 1.0 nm as shown in Fig. 3(b), which is limited by a spectral resolution of our experimental setup. The small FWHM (2.1 nm) before the lasing threshold in Fig. 3(b) is due to the narrow width of the defect mode within the band gap. The spectral narrowing above the lasing threshold is more significant if the FWHM of the lasing is compared with that of the spontaneous emission from a medium without any periodic structure (thin film of DCM in PMMA), which is about 75 nm.

The defect-mode low threshold lasing action results from the modification of the density of states and the enhanced spontaneous emission due to the placement of the gain medium within a 1D PBG structure. According to Fermi's golden rule, the rate of spontaneous emission at a frequency ω is proportional to the density of states at that frequency, $\rho(\omega)$.[21] Therefore, if the gain medium is within a photonic band gap structure, the spontaneous emission rate at a particular wavelength can be enhanced or suppressed by a factor proportional to $\rho(\omega)$. We analytically calculated the density of states for the defect-mode finite 1D photonic band gap structure shown in Fig. 1. A normalized plot of $\rho(\omega)$ with respect to the density of states in vacuum ($1/c$, c: speed of light in vacuum) is displayed in the inset in Fig. 2(a).[22] The density of states has very low values within the photonic band gap, except at the localized defect modes, where the rate of spontaneous emission is enhanced by a large factor. As the gain for the localized defect modes is greatly increased with the increased spontaneous emission rate, low threshold lasing can be accomplished if the gain threshold is reached.

In summary, we have fabricated an organic/inorganic hybrid 1D photonic crystal containing a dye doped defect layer and demonstrated low threshold defect-mode lasing. TiO_2 nanoparticles and PMMA have been employed as high and low index materials with the organic laser dye, DCM, as the gain medium. Low threshold lasing was induced at a localized defect-mode wavelength resulting from the suppressed density of states of photons within the photonic band gap and the enhanced rates of spontaneous emission at the localized resonant defect mode.

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