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Low-threshold blue-emitting monolithic polymer vertical cavity surface-emitting lasers

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The authors report on a monolithic vertical microcavity blue laser with a carbazole/fluorenyl derivative copolymer active film. The laser is realized by electron-beam deposition of the two dielectric mirrors on the bottom and on the top of the polymeric active layer. The devices exhibit a threshold fluence as low as 1.2 $\mu J/cm^2$, with a divergence of the emission beam of 2.8°. The measured lasing threshold and operational lifetimes ($>1.5\times10^4$ pulses at an excitation density 500 times larger than threshold) are among the best so far reported for blue-emitting polymer lasers, thus making these devices promising candidates for future electrical excitation. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2353822]

Since the discovery of stimulated emission (SE), amplified spontaneous emission (ASE), and lasing in conjugated polymer films,[1,2] many efforts have been directed towards the realization of cheap, multiwavelength, solid-state organic-based laser devices for diagnostic applications, displays, and data storage.[3–7] Nowadays, conjugated polymers exhibit SE in the entire visible range,[8] and organic materials for optical gain in the deep blue and UV region have been reported.[3,9] In particular, in the last few years the development of low-threshold blue-emitting lasers has represented the keystone of future high-density optical information technology. To date, such devices have been realized by slab waveguides,[10,11] distributed feedback geometries,[12–15] and microcavities.[16,17] Among the various structures exploited, vertical cavity surface-emitting lasers (VCSELs) allow one to realize (by a single-step process) multidimensional laser arrays, with low-divergence beam emitted perpendicularly to the substrate, suitable for coupling with optical fibers and telecommunication applications.

In this letter, we report on a monolithic vertical microcavity blue laser with a carbazole/fluorenyl derivative copolymer active film. The device is realized by direct electron-beam reactive deposition of the two distributed Bragg reflectors (DBRs) on the bottom and on the top of the polymeric active layer. As shown in previous studies[18,19] the suitable developed, low-temperature, reactive electron-beam deposition of oxides preserves the emission properties of the organic film, thus allowing laser emission with thresholds around 90 $\mu J/cm^2$. We here demonstrate how, by properly modifying some details of the microcavity structure (i.e., increasing the dielectric pairs constituting the mirror, changing their disposition with respect to the active medium,[20] and employing a different conjugated polymer), it is possible to further improve the lasing performances. The measured lasing threshold (1.2 $\mu J/cm^2$, i.e., 70 times lower than the previous study)[19] and operational lifetimes ($>1.5\times10^4$ pulses at an excitation density 500 times larger than threshold) are among the best so far reported for blue-emitting polymer lasers.

The bottom DBR of our polymer-based microcavity lasers was evaporated by an electron-beam gun system onto Corning quartz substrate (10×10 mm^2). This mirror was composed of 8.5 $\lambda/4$ pairs of SiO_2/TiO_2 (with refractive index contrast $\Delta n=0.86$ at 450 nm) deposited in an oxygen atmosphere at 260 °C, using 99.9% purity TiO_2 and SiO_2 as sources. After the DBR deposition, the conjugated copolymer, poly[(9,9-hexylfluorenyl-2,7-ditl)-alt-co-(9-ethyl-3,6-carbazole)] (PFC) (top inset of Fig. 1), was spin cast from chloroform solution onto the bottom mirror, and the top reflector was finally evaporated directly on the polymer film by our specifically implemented low-temperature reactive electron-beam deposition of oxides. The top DBR was composed of 10.5 $\lambda/4$ pairs of SiO_x/TiO_x ($\Delta n=0.60$ at 450 nm) deposited in oxygen pressure, at room temperature, with the only chamber heating induced by the switched-on electron gun. The confinement of the cavity photons inside the cavity layer is here promoted by both increasing the number of pairs constituting the mirrors and inducing a waveguide effect at the organic/oxide interface by sandwiching the organic layer between two SiO_x layer with low n (device scheme in the bottom inset of Fig. 1). The VCSELs were

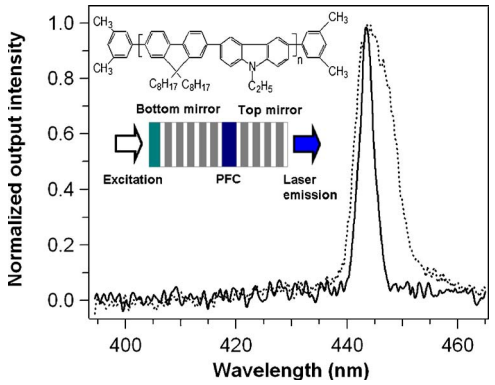

FIG. 1. (Color online) Normalized PL emission spectra of the laser device below (dashed line) and above (continuous line) threshold. Top inset: molecular structure of PFC. Bottom inset: VCSEL scheme.

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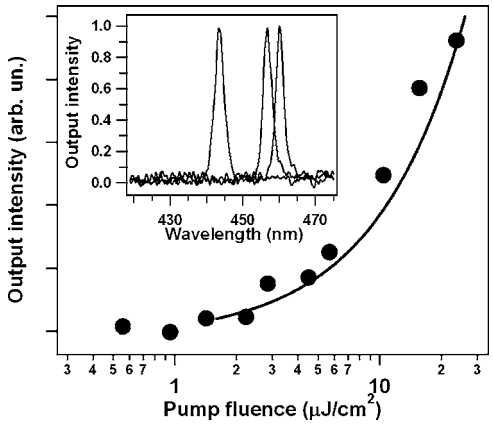

FIG. 2. Excitation fluence dependence of the laser peak output intensity. The solid curve is the linear fit to the experimental data. The inset shows the normalized laser emission spectra obtained by changing the device cavity length (excitation density of 20 μJ/cm^2).

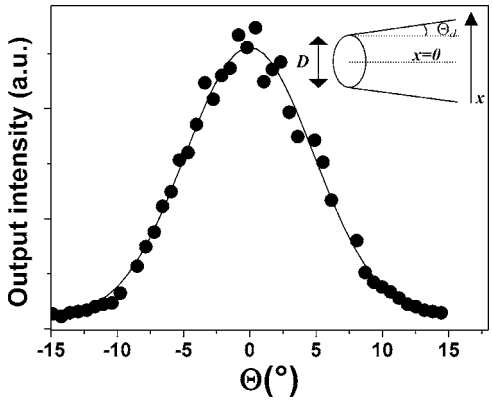

FIG. 3. Peak intensity of the emitted blue light vs the observation angle, $\Theta=\arctan(x/\delta)$, where δ is the distance between the microcavity and the detection plane. Inset: Scheme of the beam divergence. The angular divergence Θ_d of the collected laser beam is related to the x position by $\Theta_d=\arctan[(x_{\mathrm{HWHM}}-D/2)/\delta]$.

excited by the third harmonic of a 10 Hz Q-switched neodymium-doped yttrium aluminum garnet laser ($\lambda=355$ nm), delivering 3 ns pulses on the polymer, after passing through the bottom mirror (transmitting about 40% at 355 nm), in a circular spot with a diameter $D=0.8$ mm. The excitation fluences were calculated by the pulse energy per unit of area, taking into account the bottom mirror transmittance and the film absorption at 355 nm. All the optical measurements were carried out in air at room temperature.

In Fig. 1 we report the normalized photoluminescence (PL) emission spectra of the laser device, collected below (dashed line) and above (continuous line) lasing threshold. The spectrum below threshold is dominated by the emission of PFC. This is modulated by the cavity and shows a quite broad peak [full width at half maximum (FWHM)=9 nm] centered at 444 nm. Above threshold the emission narrows and shifts at $\lambda_0=443$ nm, with a FWHM of 2.7 nm. The single-mode laser emission was tuned in the whole gain region of the polymer in a range as wide as 17 nm by changing the thickness of the active layer (inset of Fig. 2). The spectra exhibit emission wavelengths $\lambda_e=443$, 456, and 460 nm (FWHM=2.7, 2.7, and 2.4 nm) for cavity thicknesses d of 139, 153, and 158 nm, respectively. Hence, being $2n\Delta d/\Delta\lambda\cong 4$, the optical cavity length L can be estimated as a number of half wavelength, $L=2\lambda/2$.

The dependence of the integrated emission intensity of the blue-emitting VCSEL on the pumping fluence is shown in Fig. 2. The input-output characteristic shows a clear threshold (TH) at $E_{\mathrm{TH}}=1.2$ μJ/cm^2. Above threshold, the emission peak grows linearly with the excitation, as expected for laser action. The SE cross section of the blue-emitting conjugated polymer, σ_{SE}, at the threshold was calculated as $\sigma_{\mathrm{SE}}=g_{\mathrm{TH}}/N_{\mathrm{TH}}$, where $N_{\mathrm{TH}}=1.4\times10^{17}$ cm^{-3} (estimated by the excitation density at threshold and by assuming a unity quantum efficiency for the emitting species) and $g_{\mathrm{TH}}\leqslant -1/(2nd)\ln(R_1R_2)=670$ cm^{-1} is the material gain at threshold. By these values we obtained $\sigma_{\mathrm{SE}}=5\times10^{-15}$cm^2 for our PFC monolithic cavity. In Fig. 3, we display the dependence of the peak intensity of the emitted light on the observation angle. The angular behavior of the laser emission is well fitted by a Gaussian function (continuous line in Fig. 3), with a FWHM divergence value $\Theta_d=2.8°\pm0.2°$.

Another challenging issue for organic-based lasers is the device lifetime,[10,13] which can be strongly reduced by the high employed excitation densities. For investigating this aspect in depth, we studied the temporal behavior of the emission intensity under excitation, for the PFC film and the VCSEL devices, respectively. The results obtained at two different pump fluences, 0.6 mJ/cm^2 (E_a) and 3.0 mJ/cm^2 (E_b), are shown in Fig. 4. Both fluences are well above the thresholds for ASE (E_{ASE}) (Ref. 21) and for lasing (E_{TH}). For both E_a and E_b, the time decay of ASE from the bare films is well described by an exponential law, $I(t)\sim e^{-t/\tau}$, with $\tau_{\mathrm{ASE},a}=240\pm5$ s and $\tau_{\mathrm{ASE},b}=55\pm1$ s, corresponding to 2400 and 550 excitation pulses, respectively. This can be rationalized by taking into account the exciton trap formation resulting from photooxidation of organic films. For instance, the light irradiation of poly(phenylenevinylene)[22] and its derivatives[23] under oxygen atmosphere determines the introduction of a carbonyl group within the polymer chains. The carbonyl sites reached by exciton diffusion act then as quenching centers for luminescence. A typical oxidation pathway is assisted by singlet oxygen, formed via energy transfer from the polymer triplet states, achieved by intersystem crossing.[24] For polyfluorene units, the photooxidation may lead to the formation of ketonic defects, i.e., of fluorenone quenching groups.[25]

In the VCSEL devices two main effects are clearly observed. First, the overall laser emission decay is much slower than that of the ASE signal, with $1/e$ decay times around 1550 and 550 s, for E_a and E_b, respectively. For very high

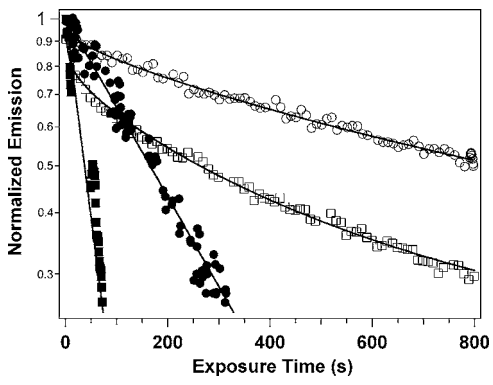

FIG. 4. Temporal behavior of the emission decay for ASE from bare films (full symbols) and from the laser devices (empty symbols) at $E_a=0.6$ mJ/cm^2 (circles) and $E_b=3$ mJ/cm^2 (squares).

excitation densities, the device life is ten times longer that the SE one from bare films. The remarkable stability of the VCSEL signal thus indicates the good encapsulation effect achieved by monolithically sandwiching the active layer between two DBRs, insulating the photoexcited region from the air atmosphere. Second, we note that the laser lifetime is governed by a multiexponential, $I(t) \sim \Sigma_{i=1,2} e^{(-t/\tau_i)^{\beta_i}}$, law. In the previous expression, $\beta_1 = 1$, $\beta_2 = 1/3$, $\tau_1 \cong 10-10^2$ s, and $\tau_2 \propto D^{-1}$, where D takes into account the diffusion of oxygen within the PFC layer, forming the excitonic traps in correspondence of randomly distributed reaction sites.[26,27] We found $\tau_{2a} = 5600 \pm 200$ s and $\tau_{2b} = 607 \pm 100$ s. The remarkable decrease observed in the VCSEL lifetime upon increasing the excitation density is consistent with the corresponding enhancement of the local heating effects induced by the pump increases, consequently increasing the oxygen mobility inside the organic layer. The local source of diffusing oxygen likely relies on the release from the DBR oxides undergoing intense UV irradiation.

In conclusion, we reported on a monolithic, organic-based VCSEL emitting in the blue spectral range for high-density storage/reading and biodiagnostic applications. The devices exhibit a threshold fluence as low as 1.2 $\mu J/cm^2$, with a divergence of the emission beam of 2.8°, and very good operational lifetimes ($>1.5 \times 10^4$ pulses at an excitation density 500 times larger than threshold). Overall, monolithic devices offer the *unique combination* of very good lasing performances, *encapsulating features* and high scalability for future integrated optics based on conjugated polymers. Laser arrays emitting simultaneously at different wavelengths can be straightforwardly realized by combining monolithic fabrication and chemical patterning approaches, such as microfluidics and ink-jet printing.

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