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We demonstrate optically excited lasing by an organic semiconducting thin-film based on 2,7-bis[4-(N-carbazole)phenylvinyl]-9,9′-spirobifluorene (spiro-SBCz) as an active gain medium with a first-order distributed feedback (DFB) reflector. We prepared DFB reflectors with periods from 132.5 to 145.00 nm and grooves from 70 to 140 nm depth by using electron–beam-lithography and plasma-etching techniques. The laser having a reflector with a 145.0 nm period had a lasing threshold of $0.72 \pm 0.07\ \mu J/cm^2$, 83% lower than its threshold of amplified spontaneous emission ($4.1 \pm 0.4\ \mu J/cm^2$).

Keywords: amplified spontaneous emission; DFB laser; e-beam lithography; reactive ion etching

INTRODUCTION

Organic semiconductor laser diodes are next-generation organic opto-electronic devices that can provide any lasing wavelength in the visible region. Unlike conventional inorganic semiconductors, organic semiconducting thin films are easily prepared using low-cost and low-temperature fabrication techniques such as vacuum deposition and spin-coating. The first amplified spontaneous emission (ASE) obtained using small organic molecules was observed in a tris-(8-hydroxyquinoline)aluminum (Alq_3) thin film doped with the highly

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fluorescent [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo [ij]quinolizin-9-yl)ethenyl]-4H-pyran-4-ylidene]propane-dinitrile (DCM2) [1]. Although lasing and ASE have also been observed in polymers [2–6] and organic single crystals under optical excitation [7,8], they have not been observed in organic molecules under electrical excitation because exciton annihilation processes occurring under high current density make the lasing threshold too high [9]. To reduce the lasing threshold enough for electrical excitation to be effective, we need to insert optical reflectors into the organic thin films. The most promising kind of optical reflector to use in films only a few hundred nanometers thick is the first-order distributed feedback (DFB) reflector, and in this report we demonstrate a first-order DFB laser using a 2,7-bis[4-(N-carbazole)phenylvinyl]-9,9′-spirobifluorene (spiro-SBCz) thin film as its active layer. We previously reported that a film consisting of spiro-SBCz doped into 4,4′-bis-(N-carbazole) biphenyl (CBP) has an ASE threshold E_{th} of only $0.11 \pm 0.05\,\mu J/cm^2$ under optical excitation, which is the lowest ASE threshold ever reported [10].

The lasing wavelength (λ_B) of DFB lasers can be derived from Bragg's law: $\lambda_B = 2\eta_{eff}\Lambda/m$, where η_{eff} is the effective refractive index, Λ is the period of the grating, and m is the order of Bragg diffraction. There have been many reports on organic semiconductor lasers with second-order ($m = 2$) DFB reflectors [6,11,12], but a second-order DFB lasers emits radiation not only in-plane but also perpendicular to the waveguide surface. Because it does not confine light as well as a first-order DFB laser does [13], its lasing threshold is higher. In this study we therefore made first-order DFB reflectors for lasers emitting in the deep-blue wavelength region. This required reflectors with a grating periodicity Λ of about 140 nm. Since it is difficult to make gratings this fine when using conventional laser-beam interference lithography [14], we instead used a direct electron beam lithography technique combined with plasma etching.

EXPERIMENTAL METHODS

We used an electron beam lithography system (JBX-5000SL, JEOL Co.) and reactive ion etching (RIE) system (RIE-10NR-K1, Samco Co.). A thermally oxidized silicon wafer substrate with a 1-μm-thick SiO_2 layer was first cleaned by ultrasonication using neutral detergent, acetone, and isopropanol. It was then treated with hexamethyldisilazane (HMDS) and spin-coated with an 85 nm-thick resist layer for electron-beam lithography (ZEP520A-7, Nihon ZEON Co.) with an electron dose optimized to 0.50 nC/cm. After the exposure the substrate was developed using a developer solution (ZED-N50, Nihon

ZEON Co.), and the development was terminated by rinsing the substrate with a rinse solution (ZMD-B, Nihon ZEON Co.). After a Cr layer 20 nm thick was deposited on the patterned resist layer by thermal evaporation under a vacuum ($\approx 1 \times 10^{-3}$ Pa), the resist layer was removed by using N-methyl-2-pyroridone, leaving a patterned Cr layer on the thermally oxidized silicon wafer. This layer was used as an etching mask while the substrate was etched with CF_4 plasma. After the etching, the Cr mask was removed in acid solution, leaving DFB reflector gratings with grooves that had periodicities ranging from 130.0 to 142.5 nm and were either 70, 110, or 140 nm depth (Fig. 1). Each of the gratings was then covered with a 50-nm-thick spiro-SBCz layer deposited under $\approx 1 \times 10^{-3}$ Pa.

The excitation light source was a nitrogen gas laser ($\lambda = 337$ nm, pulse width $\approx$500 ps, repetition rate = 20 Hz), and the excitation light was focused onto $3 \times 10^5\,\mu m^2$ area of the organic layer through a cylindrical lens and slit, and the emitted light was collected from the edge of the samples into an optical fiber connected to a spectrometer (PMA-11, Hamamatsu Photonics Co.). The size of radiation area was carefully checked by using a beam profiler (C9164-01, Hamamatsu Photonics Co.), and all measurements were made under a nitrogen atmosphere to keep the samples from being degraded by moisture and oxygen.

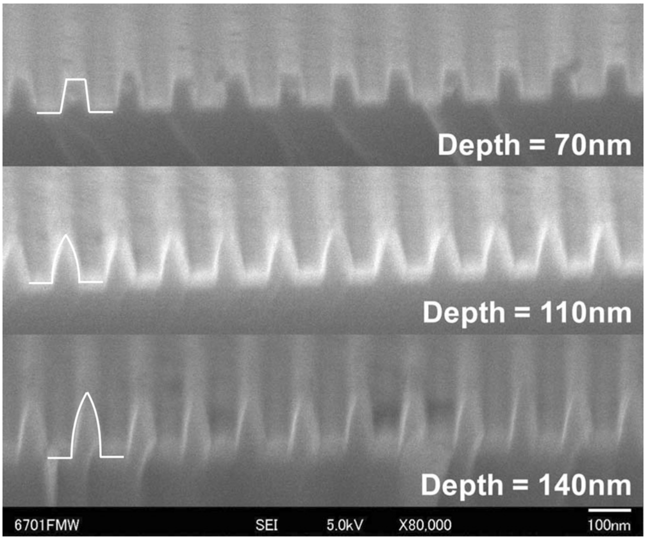

FIGURE 1 SEM cross sections of DFB reflectors with optical gratings of various depths, 70 nm, 110 nm and 140 nm.

RESULTS AND DISCUSSION

The absorption, photoluminescence (PL), and ASE spectra of a spiro-SBCz layer are shown in Figure 2 along with the molecular structure of spiro-SBCz. The PL spectrum shows three vibronic emission bands: one at 446 nm corresponding to the 0-0 transition, one at 473 nm corresponding to the 0-1 transition, and one at 504 nm corresponding to the 0-2 transition. The spiro-SBCz film shows an absolute PL quantum efficiency ϕ_{PL} of 42% and a fluorescence lifetime τ_f of 0.65 ns. Its PL spectrum and emission intensity changed dramatically increases in excitation intensity, and a clear ASE threshold E_{th} was observed at $4.1 \pm 0.4\,\mu J/cm^2$. The peak emission wavelength λ_{max} of the ASE spectrum was at 474 nm, which is very close to the wavelength of the 0-1 transition of spiro-SBCz.

The lasing characteristics of various DFB reflectors are summarized in Table 1. In the reflectors having grooves 70 nm depth, lasing occurred in samples with $\Lambda = 137.5$, 140.0, 142.5, or 145.0 nm and the lasing threshold was lowest ($0.72\,\mu J/cm^2$) for the sample with $\Lambda = 145.0$ nm. In the reflectors with grooves 110 or 140 nm depth, the lowest lasing thresholds were $2.6\,\mu J/cm^2$ in the sample with $\Lambda = 140.0$ nm and $2.4\,\mu J/cm^2$ in the sample with $\Lambda = 132.5$ nm. Thus, the lowest threshold shifted to the larger Λ with an decrease of the depths. We suppose that these differences are attributable to the shapes of the reflectors. Since the deeper grooves have a sharper

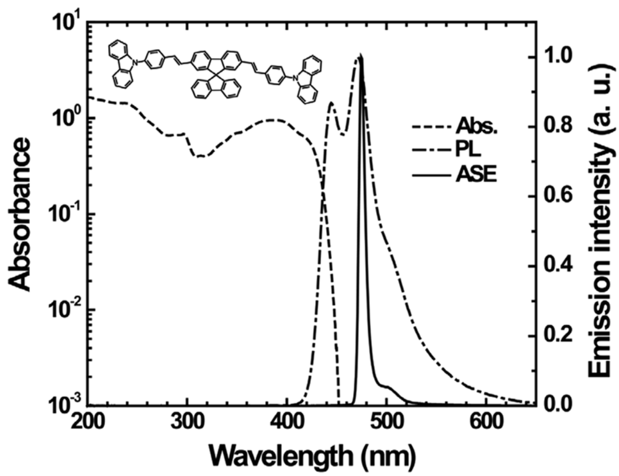

FIGURE 2 Absorption, PL, and ASE spectra of spiro-SBCz thin film. Inset: Chemical structure of spiro-SBCz.

TABLE 1 Lasing and ASE Wavelengths and Thresholds for each Sample

Depth (nm)	Λ	132.50	135.00	137.50	140.00	142.50	145.00
70	λ_{max} (nm)			467.14	470.90	474.66	479.91
	E_{th} (μJ/cm^2)			7.1 ± 0.7	1.8 ± 0.2	0.90 ± 0.09	0.72 ± 0.07
110	λ_{max} (nm)	467.89	472.40	473.15	478.41	482.92	490.42
	E_{th} (μJ/cm^2)	19 ± 2	4.3 ± 0.4	10 ± 1	2.6 ± 0.3	4.3 ± 0.4	17 ± 2
140	λ_{max} (nm)	474.66	479.92	484.42	489.68		
	E_{th} (μJ/cm^2)	2.5 ± 0.3	2.4 ± 0.2	2.9 ± 0.3	5.7 ± 0.6		

triangular structure (Fig. 1), the lasing wavelength was red-shifted with increasing groove depth, probably because the η_{eff} changed even when the reflector period was the same. Furthermore, we mention the threshold dependence on the depth. Although the reflectors having deep grooves can confine light into a waveguide effectively, our results showed the opposite tendency. One possible reason is the geometric shape of the DFB reflectors. The surface topography of the organic layer on a DFB reflector with grooves 70 nm depth is shown in Figure 3. This sample has 40-nm-depth curved structures in the organic active layer, causing scattering loss in the waveguides.

Figure 4(a) shows the PL spectrum of a spiro-SBCz thin film and the lasing spectra from the various DFB reflectors with the grooves 70 nm depth. The lasing wavelength systematically shifted from 467.14 nm to 479.91 nm when the grating period of the DFB reflectors changed from 137.5 nm to 140.0 nm. The lowest lasing threshold, 0.72 μJ/cm^2, was observed at $\lambda_{max} = 479.91$ nm in the sample with $\Lambda = 145.0$ nm, although we expect the lowest threshold occurs around the 0-1 transition. Figure 4(b) shows excitation-intensity dependence of edge-emission intensity and full width at half maximum (FWHM) in the samples with and without DFB reflectors. With increasing excitation intensity the DFB laser with $\Lambda = 145.0$ nm and grooves 70 nm depth showed a more rapid increase of emission intensity and more rapid decrease of FWHM than did the corresponding laser without the DFB reflector. The lasing threshold was 83% lower than the ASE threshold, indicating that the light was effectively fed back into the spiro-SBCz layer using the first-order DFB reflector.

To understand mechanism of the dependence of lasing threshold on lasing wavelength, we calculate the stimulated emission cross section (σ_{em}) of spiro-SBCz by using the following equations [15]:

$$\sigma_{em}(\lambda) = \frac{\lambda^4 E_f(\lambda)}{8\pi n^2(\lambda) c \tau_f},$$

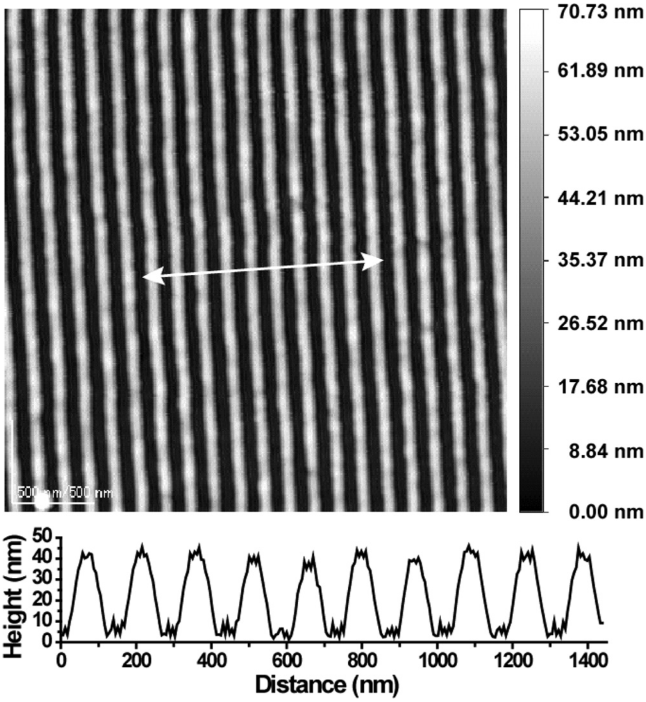

FIGURE 3 AFM image showing the topography of an organic layer with DFB reflector with grooves 70 nm depth.

and

$$\phi_{PL} = \int E_f(\lambda) d\lambda,$$

where $E_f(\lambda)$ is the fluorescence distribution, ϕ_{PL} is the PL quantum efficiency ($n_f = 0.42$), $n(\lambda)$ is the refractive index (1.8), c is the speed of light in a vacuum, and τ_f is the fluorescence lifetime (0.65 ns). The large stimulated emission cross section $\sigma_{em}(\lambda)$ $2.0 \times 10^{-16}\,\mathrm{cm}^{-2}$ was obtained at an ASE peak wavelength λ of 474 nm. The inset in Figure 4(a) shows the relation between the σ_{em} and the lasing thresholds of several samples. We observed an unusual correlation between E_{th} and σ_{em}. In spite of σ_{em} being lower at wavelengths longer than the peak wavelength, 473 nm, the lowest E_{th} was obtained at 479.91 nm. This result indicates the presence of optical loss such as self-absorption around the peak wavelength.

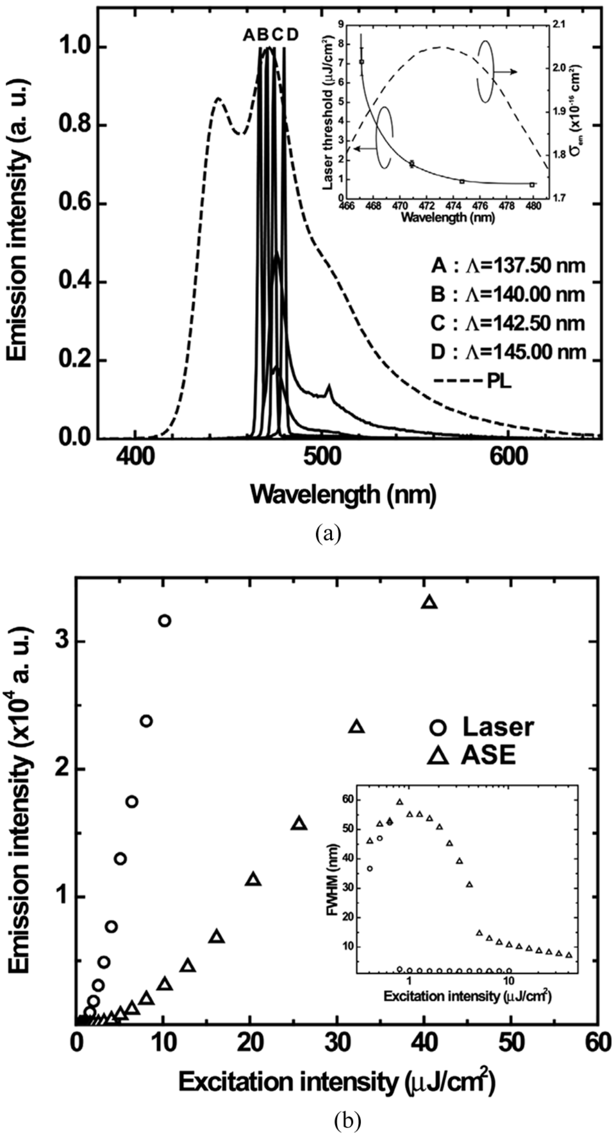

FIGURE 4 (a) Photoluminescence and lasing spectra of samples with depth of 70 nm and periods of 137.5 nm, 140.0 nm, 142.5 nm, and 145.0 nm, respectively. Inset: (- - - -) stimulated emission cross section of spiro-SBCz thin film, (——) dependence of lasing threshold on lasing wavelength. (b) Dependence of edge emission intensity on excitation intensity (○) with and (△) without an optical reflector. Inset: Dependence of FWHM on excitation intensity (○) with and (△) without an optical reflector.

SUMMARY

We prepared first-order DFB reflectors by using electron-beam lithography and plasma etching. We demonstrated control of lasing wavelength depended on the periodicity and groove-depth of the reflectors and obtained the low lasing threshold $0.72 \pm 0.07\,\mu J/cm^2$ by using a first-order DFB reflector with $\Lambda = 145.0\,nm$ and grooves 70 nm depth. This lasing threshold was 83% lower than the ASE threshold ($4.1 \pm 0.04\,\mu J/cm^2$).

REFERENCES

[1] Kozlov, V. G., Bulovic, V., & Forrest, S. R. (1997). *Appl. Phys. Lett.*, *71*, 2575.
[2] Spehr, T., Pudzich, R., Fuhrmann, T., & Salbeck, J. (2003). *Org. Elect.*, *4*, 61.
[3] Zhang, D., Zhang, S., Ma, D., Mina, G, & Li, X. (2006). *Appl. Phys. Lett.*, *89*, 231112.
[4] Sheridan, A. K., Buckley, A. R., Fox, A. M., Bacher, A., Bradley, D. D. C., & Samuel, I. D. W. (2002). *J. Appl. Phys.*, *92*, 6367.
[5] Moses, D. (1992). *Appl. Phys. Lett.*, *60*, 3215.
[6] Karnutsch, C., Gyrtner, C., Haug, V., Lemmer, U., Farrell, T., Nehls, B. S., Scherf, U., Wang, J., Weimann, T., Heliotis, G., Pflumm, C., deMello, J. C., & Bradley, D. D. C. (2006). *Appl. Phys. Lett.*, *89*, 201108.
[7] Xie, W., Li, Y., Li, F., Shen, F., & Ma, Y. (2007). *Appl. Phys. Lett.*, *90*, 141110.
[8] Losio, P. A., Hunziker, C., & Gunter, P. (2007). *Appl. Phys. Lett.*, *90*, 241103.
[9] Nakanotani, H., Sasabe, H., & Adachi, C. (2005). *Appl. Phys. Lett.*, *86*, 213506.
[10] Nakanotani, H., Akiyama, S., Ohnishi, D., Moriwake, M., Yahiro, M., Yoshihara, T., Tobata, S., & Adachi, C. (2007). *Adv. Fun. Mater.*, *17*, 2328.
[11] Ichikawa, M., Tanaka, Y., Suganuma, N., Koyama, T., & Taniguchi, Y. (2001). *Jpn. J. Appl. Phys.*, *40*, L799.
[12] Schneider, D., Rabe, T., Riedl, T., Dobbertin, T., Werner, O., Kroger, M., Becker, E., Johannes, H.-H., Kowalsky, W., Weimann, T., Wang, J., Hinze, P., Gerhard, A., Stossel, P., & Vestweber, H. (2004). *Appl. Phys. Lett.*, *84*, 4693.
[13] Carroll, J., Whiteaway, J., & Plumb, D. (1998). Distributed feedback semiconductor lasers, SPIE PRESS.
[14] Ichikawa, M., Tanaka, Y., Suganuma, N., Koyama, T., & Taniguchi, Y. (2003). *Jpn. J. Appl. Phys.*, *42*, 5590.
[15] Liu, X., Py, C., Tao, Y., Li, Y., Ding, J., & Day, M. (2004). *Appl. Phys. Lett.*, *84*, 2727.