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The authors demonstrate direct electron-beam writing on conjugated polymers as patterning route to realize plastic optoelectronic devices. Lithography was carried out by a 20 kV electron beam dose in the range of 0–360 μC/cm², with no need for masking or development/etching processes. The features could be employed for the fabrication of polymer distributed feedback lasers, exhibiting optically pumped lasing in the range of 607–620 nm, with a spectral linewidth around 1 nm and a threshold excitation fluence of 34 μJ/cm². © 2007 American Institute of Physics.

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Conjugated polymers are relevant materials for plastic optoelectronics. They show high photoluminescence (PL) quantum yields, tunable luminescence, amplified spontaneous emission (ASE) line narrowing, and large cross-sections (≈10⁻¹⁵ cm²) for stimulated emission. For their good optical gain and waveguiding properties, conjugated polymers attracted attention as solid-state lasing materials, embedded in a variety of cavity configurations. Since the emission performances of plastic photonics can be improved by incorporating wavelength-scale microstructures, patterning conjugated polymers has recently emerged as research topic. Structuring organics has been demonstrated to enhance light trapping and efficiency in photodiodes, increase luminescence yield, and improve output from organic-based light-emitting devices (OLEDs). In particular, texturing periodic nanostructures in organics, such as in distributed feedback (DFB) systems, could be achieved by plastic or inorganic substrates or by imprinting the emissive organic layer. Mainly morphological patterns were realized to produce nanostructured, organic-based photonic devices, whereas nonmorphological approaches, determining periodic optical modulation without topological contrast, were generally limited to optical phase masks. Scanning probe or optical methods to directly pattern conjugated polymers generally provided low throughput. Alternative technologies for producing devices with areas of many mm² certainly deserve to be investigated in depth.

So far, a few studies were carried out on direct maskless exposure procedures on conjugated materials. Morphological patterning of polyfluorene compounds and poly(3-octylthiophene) was obtained by electron-beam lithography (EBL), and both the polymers were found to behave like negative (cross-linking) tone resists materials upon exposure. EBL on poly[2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) was employed for producing 500 nm stripes by development in p-xylene, exhibiting mobility significantly larger than that achieved by sandwiched devices. In this letter, we demonstrate DFB lasers made by direct EBL on the conjugated polymer MEH-PPV, with no need for masking or development/etching processes. The resulting polymer lasers were found to emit in the range of 607–620 nm, with a spectral linewidth around 1 nm and a threshold excitation fluence as low as 34 μJ/cm².

Si(100) wafers with 800 nm SiO₂ coverage were employed as substrates to spin-cast 10⁻⁵ M toluene solutions of MEH-PPV (American Dye Source) at 2000 rpm for 40 s. 8.0 × 1.0 mm² gratings with period in the range of 580–610 nm were written on the sample in about 3.5 h by a Raith 150 system with acceleration energy of 20 keV, a 60 μm aperture, and doses up to 360 μC/cm². The PL spectra were measured by using a diode laser (Nichia, λ = 405 nm) as excitation source, delivering 0.1 mW onto a 400 μm spot, and a fiber-coupled charge coupled device (CCD), and the absolute PL quantum efficiency ηPL was determined by an integrating sphere. Ellipsometry measurements were performed on a 25 mm² uniformly exposed MEH-PPV area using a J. A. Woollam Co. Inc. ellipsimeter with an autoretarder and a Xe lamp. The sample was modeled as an uniaxial film on a Si/SiO₂ substrate with its optic axis orthogonal to the film surface. The spectra depend on the film thickness d, on the thickness nonuniformity dμ, and on both the refractive indices n_in-plane and n_out-of-plane in the plane of the film and along the surface normal, respectively. The latter were parametrized by the WVAJE 32 program. The experimental ellipsometry angles ψ and Δ were then fitted by the Marquardt-Levenberg algorithm, allowing us to determine n_in-plane and n_out-of-plane. The DFB devices were pumped by a Q-switched Nd doped yttrium aluminum garnet laser (2 ns pulses, repetition rate of 10 Hz) under vacuum at about 10⁻⁵ mbar.
In order to assess the influence of EBL on the polymer optical properties, we collected the absorption and fluorescence spectra of MEH-PPV before and after lithography (Fig. 1(a) and Table I). Both absorption and PL show a blueshift of the peak wavelengths ($\lambda_{\text{abs}}$ and $\lambda_{\text{PL}}$) of about 11 and 4 nm, respectively, after exposure by 150 µC/cm². The absorption and emission spectra are largely unchanged, with a slight increase of the full width at half maximum (FWHM), whereas $\eta_{\text{PL}}$ decreases from 52% to about 30% after EBL exposure. We observed a decrease of the emission intensity and blueshift of $\lambda_{\text{PL}}$ upon increasing the EBL irradiation dosage in the range of 0–360 µC/cm² [Fig. 1(b)], with a $\lambda_{\text{PL}}$ reduction up to 7 nm with respect to the native polymer. We also compared the optical gain of native and irradiated films by analyzing ASE from the sample edge under pumping with UV pulsed laser light ($\lambda=355$ nm). We found that the electron-beam exposure suppresses the polymer ASE [inset of Fig. 1(b)], no gain-narrowing being observable from irradiated samples even for pumping fluences up to the film ablation threshold ($\approx 10$ mJ/cm²).

Figure 2 shows the behavior of the ellipsometry angles $\psi$ and $\Delta$ as measured at several angles of incidence (dashed lines) on the film before the exposure. The resulting in-plane and orthogonal refractive indices take values from 1.86 to 1.69 and from 1.62 to 1.54 between 600 and 900 nm, respectively. We could not appreciate changes of the refractive index in this spectral range, since both the $n_{\text{in-plane}}$ and $n_{\text{out-of-plane}}$ were found to coincide, within an experimental error (±0.02) before and after EBL (Table I).

The impact on luminescence suggests that the polymer average conjugation length decreases upon EBL. In particular, the scission of C–H bonds can determine the increase of orientational and conformational disorder in organics, causing a fragmentation of the conjugation within the material. In addition, cross-linking could be induced by the electron irradiation of the alkyl side chains, whose cleavage and subsequent partial polymerisation can induce volumetric reduction of the exposed polymer regions.26 This was confirmed by the resulting solubility of exposed MEH-PPV in toluene in which the polymer behaves like a negative type resist.

The surface morphology of MEH-PPV samples, textured with 610 nm period gratings at different EBL doses, was investigated by atomic force microscopy (AFM) (Fig. 3). Broad, smooth elevated areas (of typical extension of 2–5 µm and height of 5–7 nm) are appreciable on the surfaces, due to the disuniformity of the spin-coating coverage. Upon irradiation a slight, periodic morphological modulation with 350 nm features appears on the films, without any development procedure. We appreciated a volumetric reduction in the exposed polymer region, with depth between 0.5 and 1.0 nm [inset of Fig. 3(d)]. We notice that, as a consequence of the influence of EBL on the material conjugation length and cross-linking, also refractive index changes below our experimental error (i.e., in the range of $10^{-4}$–$10^{-5}$) are likely and can affect waveguiding in the exposed polymer, as previously observed in lithium fluoride crystals.28,29

This approach allows one to overcome problems related to resist development. For instance, the profile of developed line features very often becomes trapezoidal25 because of the lack of a sharp threshold in the solubility contrast between irradiated and nonirradiated polymer regions. Nonmorphological gratings in conjugated polymers could also be advantageous for OLEDs embedding nanostructures, since, for being fully compatible with the deposition of electrodes (without causing electrical disconnections because of topo-

![FIG. 1. (a) Absorption and time-integrated PL spectra of MEH-PPV before (empty circles and squares, respectively) and after (superimposed lines) EBL. The vertical arrows indicate the observed blueshift of the spectra after exposure. (b) PL intensity (squares, left vertical scale) and peak wavelength (circles, right vertical scale) vs EBL dose. Inset: ASE spectra from native (full line) and irradiated (dotted line) MEH-PPV films.](image)

![FIG. 2. Ellipsometry data: $\psi$ and $\Delta$ as measured (dashed lines) or generated by the fitting (dotted lines) at different angles of incidence from 35° to 75° on pristine MEH-PPV film on a Si/SiO₂ substrate, and in-plane and out-of-plane refractive indices of the film as deduced by fitting.](image)

### TABLE I

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{PL}}$ (nm)</th>
<th>$\Delta\lambda_{\text{PL}}$ (nm)</th>
<th>$\lambda_{\text{abs}}$ (nm)</th>
<th>$\Delta\lambda_{\text{abs}}$ (nm)</th>
<th>$\eta_{\text{PL}}$ (%)</th>
<th>$n_{\text{in-plane}}$ (607 nm)</th>
<th>$n_{\text{out-of-plane}}$ (607 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before EBW</td>
<td>580</td>
<td>77</td>
<td>483</td>
<td>125</td>
<td>52</td>
<td>1.84±0.02</td>
<td>1.62±0.02</td>
</tr>
<tr>
<td>After EBW</td>
<td>576</td>
<td>83</td>
<td>472</td>
<td>136</td>
<td>30</td>
<td>1.83±0.02</td>
<td>1.61±0.02</td>
</tr>
</tbody>
</table>
logical step profiles) and of organic layers, active lasing films should be preferentially flat.

We employed the MEH-PPV gratings for realizing DFB lasers. Figure 4 shows the emission spectra by a grating period (Λ) of 580 nm, exposed by 150 μC/cm². At excitation fluence below 30 μJ/cm² the PL is featureless, with FWHM around 20 nm, which is remarkably narrower than the linewidth of the cw PL of the native polymer (Δλ PL = 77 nm, Table I), indicating that a spectral selection is induced by the exposed pattern. For higher pump energies, a single narrow peak (λ m = 607 nm, FWHM ~ 1 nm) dominates the spectrum (squares in Fig. 4). The emission is highly polarized, with the electric field parallel to the grating lines, corresponding to transversal electric guided modes (polarization ratio of 100:1). The threshold excitation fluence was measured to be 34 μJ/cm² (inset of Fig. 4). According to the Bragg expression, mλ eff = 2n eff Λ (m indicates the diffraction order), the discrepancies between the grating period and λ m are related to the ratio n eff/m. In our case, n eff is estimated around 1.6 for the nonmorphological grating, and the device works at the third order. The lasing wavelength could also be tuned within the polymer gain-narrowing spectral range by changing Λ. A grating period of 610 nm resulted in a DFB emission at 620 nm, with a lasing threshold of 113 μJ/cm² (Fig. 4).

In conclusion we demonstrated EBL on a conjugated polymer for the one-step realization of organic DFB lasers. As demonstrator, we present a single-mode, highly polarized DFB laser emitting at 607 nm with 34 μJ/cm² threshold.

FIG. 3. (Color online) Surface morphology of MEH-PPV patterned by EBL at (a) 120, (b) 180, (c) 210, and (d) 300 μC/cm², investigated by AFM. Grating period of 610 nm. Vertical scale of 15 nm and scan size of 9.0 × 9.0 μm². Inset of (d): AFM cross section of the profile (Z vs X) of the exposed stripes along the continuous line shown in (d).

FIG. 4. DFB emission spectra below and above threshold (26 μJ/cm², solid curve and 380 μJ/cm², full squares) with Λ = 580 nm, and DFB spectrum above threshold with Λ = 610 nm (full circles). Inset: DFB peak emission intensity vs absorbed excitation fluence for Λ = 580 nm (squares) and 610 nm (circles). The solid lines are linear fits to the experimental data.