

Improved operational lifetime of semiconducting polymer lasers by encapsulation

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We report polymer distributed feedback lasers with dramatically extended operational lifetimes by using a simple encapsulation process. The lasers are configured as surface emitting, two-dimensional distributed feedback lasers based on the polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene]. The microstructure is transferred to the polymer surface through solvent assisted micromolding. Once encapsulated, a 2500-fold improvement in lifetime is demonstrated under ambient conditions, compared to the unencapsulated device. A blueshift of the emission wavelength observed during operation is characterized by absorption and ellipsometry measurements and attributed to a change in effective index due to a loss of conjugation in the polymer. © 2007 American Institute of Physics. [DOI: 10.1063/1.2826276]

Since the demonstration of lasing from a semiconducting conjugated polymer,¹ the development of lasers based on these fascinating materials has been a vigorous research topic. Their large gain cross sections coupled with broad emission spectra and ease of processing from solution, make conjugated polymers particularly suited to the fabrication of photonic devices.²⁻⁴

The most common resonators now used are diffractive structures that incorporate wavelength scale microstructure to form distributed feedback (DFB) lasers. The corrugation can be etched into a silica substrate⁵ or patterned directly into the polymer film using a soft lithographic method such as solvent assisted micromoulding^{6,7} (SAMiM). In both cases, the high refractive index contrast of the microstructured interface can allow for very strong feedback in a compact device.⁸

A significant challenge for the application of these devices is to develop configurations which achieve adequate stability. One limitation of these materials is their susceptibility to degradation in the presence of oxygen and water. To date, there is little quantitative data on the operating lifetimes of organic semiconductor lasers.⁹⁻¹¹ While a few polymer lasers have included a thin passive polymer cover layer,^{12,13} the quantitative effect on lifetime was not discussed. Using encapsulation to extend operational lifetime is commonplace in the field of organic light emitting diodes (OLEDs), protecting the emissive polymer layer and metal contacts from oxidation. In the case of OLEDs, encapsulation is typically applied on top of the metal cathode so properties of the device are largely unaffected with little impact on the external quantum efficiency or the photoluminescence spectrum.¹⁴ For DFB lasers, more care must be exercised when selecting encapsulating materials. Changes to the refractive index contrast between layers can have a dramatic effect on the waveguide modes of the device. The encapsulating layers should also be optically transparent and not react adversely with the polymer while still acting as an effective atmospheric barrier.

In this letter, we show that a polymer laser can be encapsulated without degrading its performance when compared to an unencapsulated laser. Absorption and ellipsometry data are used to quantify photodegradation effects occurring within the polymer during extended device operation. We also demonstrate substantial improvements to the operating lifetime of the encapsulated laser compared to the unencapsulated case when operating under ambient conditions.

The polymer DFB laser structure studied comprised a silica substrate ($12 \times 12 \text{ mm}^2$) coated with a thin film of the polymer poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) via spin coating. A two-dimensional "egg box" corrugation was patterned into the MEH-PPV film using SAMiM from an elastomeric copolymer stamp,¹⁵ which was wetted with chlorobenzene. The resulting grating covered $>80\%$ of the polymer surface, with a period of 400 nm and depth of ~ 50 nm. In-plane feedback and surface-emitted output coupling were provided by second and first order Bragg scattering, respectively.

To perform the encapsulation, a commercially available optical adhesive (Norland 68) was used. This provided uniform coverage of the microstructured MEH-PPV film, maintaining a good index contrast ($\Delta n = 0.32$ at $\lambda = 630$ nm) while being optically transparent. The adhesive was degassed prior to use via a freeze-thaw degassing technique and was drop cast directly onto the MEH-PPV surface. A silica coverslip ($150 \mu\text{m}$ thick) was then placed on top of the adhesive. The entire structure was finally UV cured (UVLMS-38 lamp, power = 8 W, $\lambda = 365$ nm) for 3 min. The lamp to sample distance was ~ 5 cm. Device structures, for the basic nonencapsulated and encapsulated lasers, with associated field profiles are shown in Fig. 1. The encapsulated DFB waveguide supports a nearly symmetrical field profile. This means that, in the encapsulated device, the electric field is stronger at the corrugated interface, compensating for the lower refractive index contrast and giving similar lasing properties for the two structures.

The lasers were optically pumped in air using the second harmonic of a passively Q -switched Nd:YVO₄ microchip laser (Alphalas GmbH) which produced ~ 1 ns pulses at

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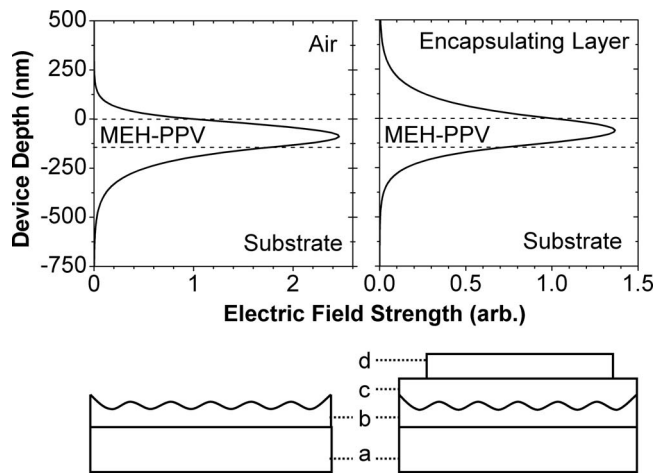


FIG. 1. Device structures and field profiles for unencapsulated (left panels) and encapsulated (right) polymer lasers. Both devices consist of (a) a silica substrate and (b) a MEH-PPV film. (c) An optical adhesive is applied to the encapsulated device and (d) covered by a layer of silica.

532 nm with a frequency of 5 kHz. The output power of the pump was modified by using calibrated neutral density filters. The laser was focused to a spot size of $\sim 10 \mu\text{m}$ radius on the top surface of the device, allowing devices to be tested under very intense pumping. Laser emission was recorded through the substrate during continual pumping of a single region of the polymer film. The spectral output was measured close to normal incidence using a fiber-coupled charge-coupled device spectrometer.

We found that the output from the unencapsulated polymer laser (emission wavelength=631 nm) when pumped at 5 kHz was extremely unstable, decaying rapidly over a period of several seconds of pumping. We, therefore, reduced the repetition frequency to 80 Hz. At a pump energy of 250 nJ/pulse, the device operated continuously for $\sim 6 \times 10^3$ pulses while decaying to 50% [Fig. 2(a)] of the initial laser intensity (~ 75 s operating time) during which time there was no shift of the emission wavelength.

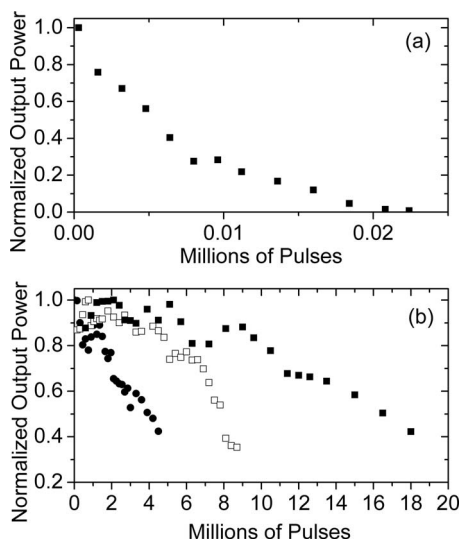


FIG. 2. Normalized output power as a function of total number of incident pulses for (a) the unencapsulated laser and (b) the encapsulated lasers for a range of excitation energies (filled circles=1 $\mu\text{J}/\text{pulse}$, open squares=500 nJ/pulse, filled squares=250 nJ/pulse).

The performance of an encapsulated device for a range of pump intensities (frequency=5 kHz) can be seen in Fig. 2(b). The initial lasing wavelength was $\lambda=639$ nm with a threshold of 25 nJ. At maximum pump energy (1 $\mu\text{J}/\text{pulse}$), the encapsulated device had decayed to 50% of its initial power after 4×10^6 pulses, corresponding to 15 min of continuous operation at ~ 40 times threshold. Laser lifetime increased to 8×10^6 (30 min operation) and 1.6×10^7 (1 h operation) pulses for decreased pump energies of 500 and 250 nJ/pulse, respectively. While encapsulating the device has little effect upon the optical properties compared to the nonencapsulated laser, for the same pump energy (250 nJ/pulse), the lifetime of the device (as number of incident pulses) has increased by a factor of >2500 . The lifetime of our encapsulated device operating in air is similar to the best previously reported result by Heliotis *et al.*⁹ for a DFB polymer laser operating in vacuum, demonstrating the effectiveness of encapsulating the polymer device. The lifetime values also compare well to Alq₃-4-dicyanomethylene-6-(pdimethylaminostyryl)-2-methyl-4H-pyran (DCM) lasers¹¹ and solid-state dye lasers, which typically exhibit lifetimes of 10^5 – 10^6 pulses. The lifetime of 1.6×10^7 pulses is equivalent to a total absorbed energy per mole (of repeat units) of 20 TJ/mol, which is an order of magnitude higher than values reported for pyromethane dyes.¹⁶

By reducing the pump frequency to 80 Hz (250 nJ/pulse), the encapsulated laser lifetime from a single region of film was almost 40 h, ~ 1600 times better than the unencapsulated device. Considering the region being pumped is $\sim 20 \mu\text{m}$ in diameter and the patterned area available for lasing is $\sim 1 \text{ cm}^2$ (i.e., $>10^5$ possible sites) there is the potential to develop practical polymer lasers with thousands of hours operation simply by scanning the pump beam. Indeed, encapsulated lasers that we have fabricated using the above method continue to operate after being stored in air for over a year. We note that our test conditions are harsh in the sense that the excitation density ($\sim 250 \text{ mJ}/\text{cm}^2$) is approximately six orders of magnitude higher than the lowest thresholds reported.⁴ Thus, by pumping larger areas of the DFB structure, much lower pumping densities can be used than in the current work^{5,9,10} which, following the trend in Fig. 2(b), should lead to further improvements in operating lifetime.

An understanding of the degradation processes occurring during extended operation may be helpful in further improving device lifetime. During the device testing, we observed that the emission wavelength underwent a blue-shift of $\sim 0.2 \text{ nm}/10^6$ pulses as the polymer film degraded [Fig. 3(a)]. If we consider the Bragg relationship, given by $m\lambda = 2n_{\text{eff}}\Lambda$, where Λ is the corrugation period, λ is the emission wavelength, m is an integer representing the order of the grating (here, $m=2$), and n_{eff} is the effective waveguide index, then the observed progressive blueshift in emission wavelength could be explained by a corresponding reduction in effective index.

To investigate this explanation further, we measured the effect of pulsed optical pumping on the absorption and refractive index of planar MEH-PPV films. Two films were spin coated onto fused silica substrates under identical conditions, giving film thicknesses of $94 \pm 3 \text{ nm}$, as derived from variable angle spectroscopic ellipsometry (VASE). Film 1 was placed in a vacuum (10^{-4} mbar) for 10 min without illumination followed by an hour illuminated by the output of

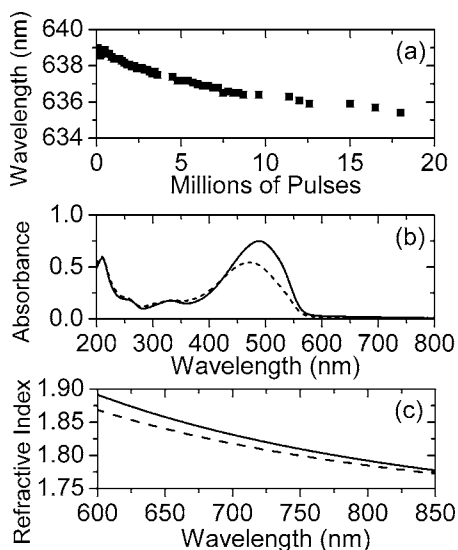


FIG. 3. (a) Change in the emission wavelength with number of incident laser pulses (250 nJ/pulse) for the encapsulated laser from Fig. 2(b). (b) Absorption spectra of the test sample (film 1) before (solid) and after (dashed) a 1 h exposure to the laser. (c) Index of refraction for the control sample immediately after fabrication (solid line) and for film 1 after exposure (dotted line).

an optical parametric oscillator (40 $\mu\text{J}/\text{pulse}$, 10 Hz, $\lambda = 532$ nm, spot diameter ~ 10 mm). Film 2 was also placed under vacuum for the same time period but without any laser exposure, as a control sample. VASE and absorption data were recorded in ambient air for both samples immediately after spin coating, and again after the time in vacuum. For this experiment, the films were not encapsulated (hence, the requirement for vacuum) to allow more accurate modeling of VASE data. The refractive indices of the films, for wavelengths between 600 and 1700 nm, were calculated from a combination of the VASE data and normal incidence transmission using a two-coefficient Cauchy model. To reduce parameter correlation problems (as a limited number of samples were measured, preventing a multisample analysis being performed^{17,18}), VASE data were analyzed assuming the films to be isotropic. A more precise analysis would require optical anisotropy to be taken into account.

Figure 3(b) shows the absorption spectra for film 1 measured before and after exposure. Initially, the absorption spectra of films 1 and 2 were nearly identical, with a strong lowest energy peak at 488 nm. After 1 h under vacuum, the absorption of control film 2 was reduced by $<1\%$, whereas for film 1, laser exposure led to a strong reduction in magnitude (45%), and a 16 nm blueshift, of the lowest energy peak. Figure 3(c) shows that these changes are accompanied by a reduction in refractive index for all wavelengths. At a wavelength of 635 nm, we observe a 0.017 reduction in polymer index. Assuming a similar level of photodegradation in the encapsulated lasers, this would lead to a blueshift in the lasing mode of ~ 3 nm, in reasonable agreement with our observed value.

The low-energy band in PPV derivatives has been assigned to transitions between delocalized π bands.¹⁹ Therefore, the changes in absorption in film 1 strongly suggest that the conjugated π -electron system has been degraded. Similar

observations have been made in previous photodegradation studies of MEH-PPV and other conjugated polymer films,^{20–23} and were assigned to the formation of carbonyl groups in the presence of oxygen.^{20–22} However, studies in ultrahigh vacuum²³ do not show carbonyl formation and the changes observed are assigned to cross linking of the polymer chains. We propose that the same processes are responsible for the behavior of our lasers. The rapid degradation of the unencapsulated device in air is assigned to carbonyl formation, whereas the much slower degradation of devices that are encapsulated or in vacuum is due to cross linking. We note that the 45% reduction in absorption in the latter case accounts for much of the loss of laser output. Further improvements in operating lifetimes may be possible by using materials less susceptible to photoinduced cross linking.

In conclusion, we have demonstrated that through encapsulation, the lifetime of a polymer DFB laser operating in air can be extended by a factor of more than ~ 2500 when compared to an unencapsulated laser. During operation, photodegradation results in a wavelength shift of the laser emission toward the blue. Through absorption and ellipsometry data, a reduction in the effective index of the device can be attributed to breaking of double bonds along the polymer backbone by photoinduced cross linking.

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