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ARTICLE *in* ADVANCED MATERIALS · FEBRUARY 2011

Impact Factor: 17.49 · DOI: 10.1002/adma.201003108 · Source: PubMed

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Elastically Tunable Self-Organized Organic Lasers

Patrick Görrn, Marcus Lehnhardt, Wolfgang Kowalsky, Thomas Riedl, and Sigurd Wagner*

Since the demonstration of lasing in organic solid-state thin-films, much effort has been devoted to this field. [1–4] Organic lasers in general offer broad tuning ranges and only a few active materials are needed to cover the entire visible spectrum.[5,6] Electrically pumped organic lasing still remains the ultimate scientific goal, which is driving significant work to address this challenge.[7–10] On the other hand, there are applications where optically pumped organic lasers might be favorable because they are easy to fabricate and require no elaborate device processing. In particular, organic lasers pumped by an inorganic laser diode,[11] or even a light emitting diode,[12,13] have recently received considerable attention. With reports of their use ranging from explosives detection[14,15] to lab-on-a-chip biospectroscopy,[16,17] organic lasers today address a broad scope of applications.

A very compact setup of an organic laser is achieved using a distributed feedback (DFB) geometry. The period of the DFB resonator and the effective refractive index set the lasing wavelength.

Therefore, there is the prospect that "soft" DFB lasers could be optically tuned on every spot of the surface simply by mechanical stretching. This feature would launch a wide range of novel applications. Aside from applications in biology, pharmaceuticals, and chemistry, other applications such as conformable sensitive optical skins for the monitoring of the structural health of civil infrastructure are imaginable.

We present a fundamentally new approach to form DFB gratings on the surface of elastomeric poly(dimethylsiloxane) (PDMS) by self-organization. Hard skins compressed by their soft substrates exhibit wrinkles, whether as deposited films[18] or as plasma-hardened surfaces[19]. Such wrinkles are common: they are created without order, vary in size and orientation, and contain defects and cracks. In contrast, we have achieved wrinkles so precisely periodic and parallel that they form sinusoidal DFB gratings. The DFB resonators have well-controlled periodicity, low dislocation density, and enable organic lasers with thresholds as low as 28 μJ cm^{-2}. At the same time, uniaxially stretching the laser by 2.2% continuously tunes its emission wavelength from 633.6 nm to 638.3 nm (4.7 nm). Mechanically, the lasers can be stretched by about 10% and therefore they have a potential tuning range of up to 20 nm if mode-hopping can be avoided.

We present how the gratings are prepared and how the organic gain medium is placed on top of the gratings. The characteristics of the resulting lasers will be shown first in the relaxed state and then during stretching. We finish by placing our results in the context of earlier work and discuss the potential for further improvements.

To fabricate self-organized gratings, the PDMS elastomer was prestretched, oxygen plasma treated to harden its surface, and then again relaxed. During relaxation of the PDMS its plasma-hardened skin was compressed and buckled to waves. The waves organize themselves into a highly ordered grating. A process that prevents the formation of cracks in the grating was developed. Cracking during the plasma treatment was avoided by keeping the oxygen pressure at a low 30 mTorr. At this pressure, the critical dose for the onset of cracking lies at around 50 J cm^{-2},[20] which exceeds the doses used to prepare the gratings. Cracking during relaxation was avoided by laminating and thereby confining the PDMS membrane to a polyimide support foil. The PDMS/foil sample was bent to a defined radius, so as to stretch the PDMS surface. Releasing the bent sample after plasma treatment was not accompanied by lateral Poisson expansion and therefore did not crack the grating. Depth and period of the grating could be tuned by altering the plasma parameters.

The self-organized gratings contain dislocations, one of which is shown in the atomic force microscopy image in **Figure 1**a. A high areal density of dislocations (n_D) in a DFB grating raises the lasing threshold power. Therefore, we explored the process parameters for grating formation that minimize n_D. As seen in Figure 1b, n_D turns out to be governed only by the oxygen plasma dose. Raising the dose decreases n_D but also, and undesirably, increases the grating period Λ.

The other parameters (listed in Figure 1b) did not affect n_D, but did affect Λ. Therefore, these "secondary" parameters were optimized to maximize the plasma dose and hence to obtain the desired grating period Λ (see Experimental Section for optimized secondary parameters). The organic lasers were realized with gratings of Λ = 420 nm and a minimized dislocation density of $n_D \approx 1.2 \times 10^4$ mm^{-2}.

An atomic force microscopy image of such a grating in the surface of PDMS is shown in **Figure 2**a. For comparison, we separately prepared cast and cure gratings by replicating a SiO_2 master grating (prepared by electron beam lithography) with rectangular gratings having five different periods between 380 nm and 420 nm and a depth of 100 nm.

The laser was fabricated by spin-coating an organic gain medium on top of the gratings. The gain medium was a guest/

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DOI: 10.1002/adma.201003108

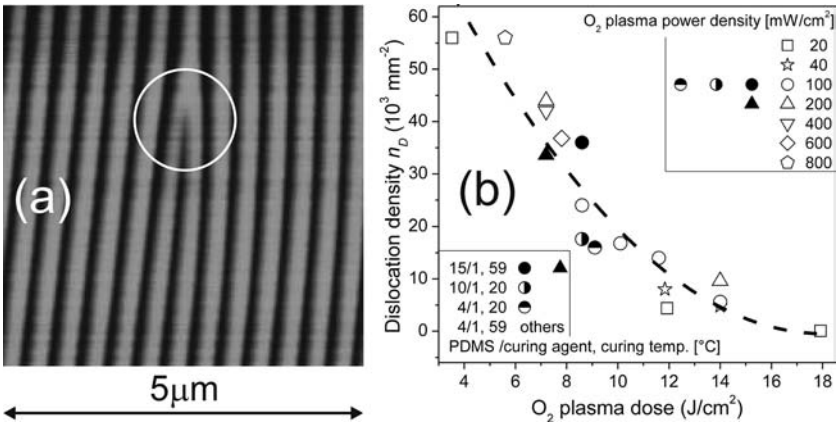

Figure 1. a) Dislocation (white circle) in a self-organized grating in PDMS. b) Density of dislocations as a function of process parameters for the preparation of the gratings: the oxygen plasma dose is evidenced as the predominant parameter.

host system of poly[2-methoxy-5-(2-ethylhexyloxy)]-1,4-phenylenevinylene (MEHPPV) doped in poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT). This medium supports lasing between 592 and 690 nm. [10] A 120-nm-thick F8BT/MEHPPV (16 wt%) layer was spin-coated from a chlorobenzene solution on both the self-organized and the replicated DFB gratings.

Stripes of these lasers were mounted grating side down in an apparatus for the uniaxial stretching of the samples. The lasers were excited through the PDMS substrate using a Q-switched, frequency-tripled solid-state laser emitting at 355 nm.

The inset of **Figure 3** shows a typical emission spectrum of the organic laser on a self-organized grating. The spectral bandwidth is less than the spectral resolution of our spectrometer (1.8 Å). Laser output power versus energy density of the pump pulse is shown by the black curve (Figure 3), which reflects a lasing threshold of 28 μJ cm^{-2}. The lowest threshold value observed on self-organized gratings was 10 μJ cm^{-2}. The threshold of the cast and cure gratings was as low as 2.5 μJ cm^{-2}.

The organic lasers were mechanically stretched by up to 10%. **Figure 4** shows how the laser emission wavelength varied with applied strain. The self-organized laser was continuously tuned from 633.6 nm to 638.3 nm (4.7 nm) by stretching by 2.2%. Stretching the cast and cure laser by 2.84% continuously tuned the wavelength from 627.7 to 629.7 nm (2.0 nm). It is important to note that the large applied strains did not destroy the laser. Instead, the lasing wavelength jumped to another continuous tuning range of up to 3% before the next jump (mode-hopping). Such mode-hopping was observed for both types of gratings. Even though the grating amplitude decreased upon stretching, the threshold for both types increased by at most a factor of 5 when stretched from 0% to 10%. The stretchability of the self-organized gratings of up to 10% opens the prospect for organic lasers having a tuning range in excess of 20 nm.

Historically, dye lasers relied on liquid dye solutions. With the demonstration of the first DFB laser, which was based on a solid dye, organic lasers became portable.[21] However, the tunability that is desired to make use of the large gain bandwidth of the dyes thereby became problematic. The emission wavelength, $\lambda \propto n_{\text{eff}}\Lambda$, of the organic DFB laser is tunable only if the period Λ of the DFB resonator or the effective index n_{eff} of the waveguide can be varied. Therefore, wavelength tunability of organic lasers on rigid gratings has been achieved only by exciting different spots on a given substrate, exploiting variations in the grating period or organic layer thickness.[22,23] This technique for tuning is not practical, as a particular position on the substrate emits a specific wavelength that cannot be varied. To tune the period, the grating must be stretched, but rigid gratings, even

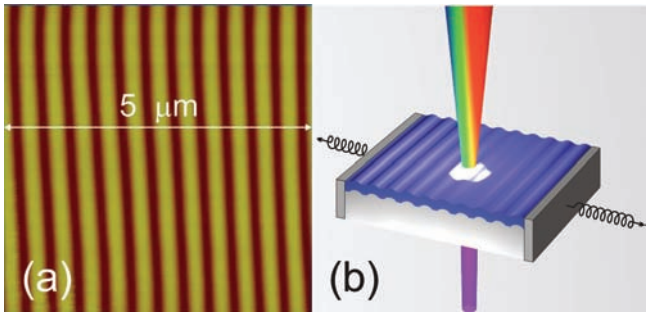

Figure 2. a) AFM image of self-organized PDMS grating. b) Schematic of the elastically tunable organic DFB laser (after removing the Kapton foil). The wavelength of the surface emitting second-order laser is tuned (symbolized by beam of changing color) by mechanically stretching the substrate. The beam of the pump laser is directed at the organic gain medium from the underside of the PDMS substrate. Spot size and divergence of the laser beam shown for illustration only.

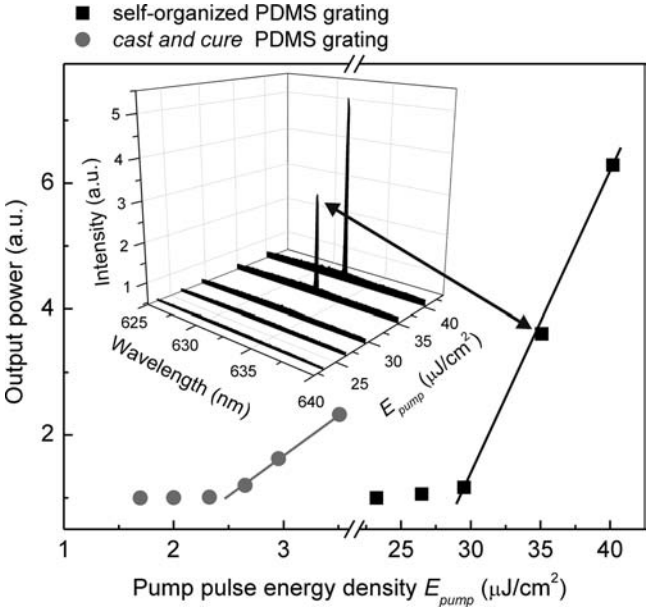

Figure 3. Output power as function of pump pulse energy density for self-organized and cast and cure gratings. The inset shows the corresponding spectra of the self-organized laser.

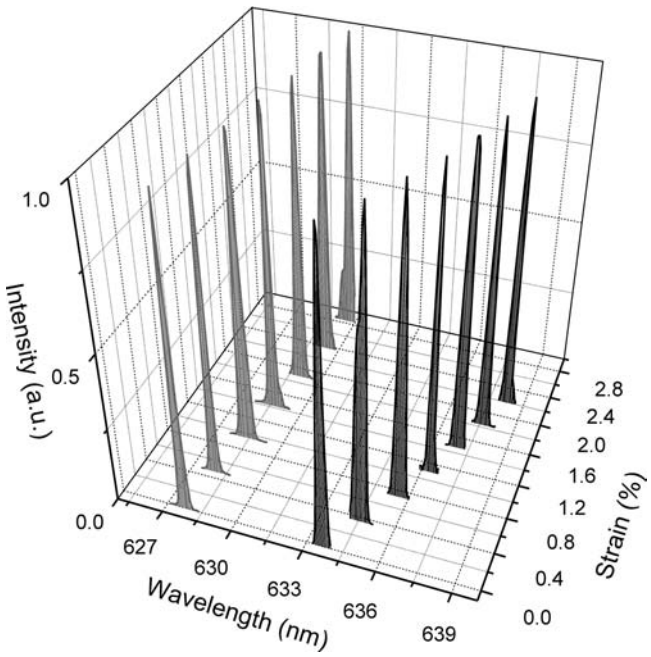

Figure 4. The DFB-lasers on self-organized (black) and cast and cure gratings (gray) are tuned by straining the PDMS substrate.

when placed on an elastomeric substrate, crack at a few percent of strain.[24] However, high-quality stretchable DFB gratings can be prepared by transferring relief patterns from rigid into soft material by a cast and cure technique, as shown above.[25,26]

By employing self-organization, we now introduce a fundamentally new approach to the preparation of DFB gratings. Spontaneously formed patterns on PDMS surfaces have been studied since Bowden et al. deposited gold films of thickness h_f and elastic modulus E_f on PDMS that was held under tensile prestrain.[18] When the prestrain was released, the surface wrinkled in sinusoidal patterns with period $\Lambda \propto h_f E_f^{1/3}$, larger than one micrometer. These periods are too long for low-loss visible light DFB resonators. Yu et al. demonstrated that these periodic structures can in principle be used as diffraction gratings for spectroscopy.[27] Small periods can be obtained by making surface layers of softer material (smaller E_f) than the gold used by these authors. PDMS surfaces can be hardened gradually by controlled oxidation, which on stretched PDMS creates submicrometer period patterns.[19,28,29] However, to-date the preparation of these patterns always has been accompanied by the formation of cracks. Cracks render the patterns useless for optical gratings because they scatter light and distribute mechanical strain non-uniformly.

The new approach completely prevents cracking and minimizes the dislocation density. In principle, DFB gratings so made can be realized on almost arbitrarily sized substrates. They enable tunable laser emission from a single, spatially well-defined substrate position. This is essential to the precise sensing of local mechanical strain and to applications that require massive parallelism. For example, lab-on-a-chip spectroscopy for high-throughput screening may employ optical absorption spectroscopy of novel biomarkers with narrow spectral absorbance.[30] In even more demanding surface-enhanced Raman spectroscopy the signal enhancement can vary by orders of magnitude upon a slight variation of the wavelength.[31]

These results show that self-organized DFB lasers made of soft materials can be tuned by stretching. We consider our results to be just the beginning of a new technology and see the opportunity for improvement in several directions. Because lasers on both self-organized and replicated gratings show mode-hopping, this effect cannot be caused by dislocations. We believe that the mode-hopping results from poor adhesion of the organic active laser material to the PDMS. Experiments with adhesion layers will show if this is the case.

The optical tuning range of the self-organized lasers is 65% smaller than the mechanical strain range. This phenomenon is even more severe for the lasers based on the cast and cure gratings. This limited wavelength tunability has two identifiable causes. One is the reduction of the effective refractive index, n_{eff}, with increasing wavelength by dispersion. The other cause is the reduction of the thickness of the waveguide by stretching, which leads to a further reduction in n_{eff}. In an approximation, we estimate that dispersion reduces the optical tuning range by 27% and the thickness reduction by 15% (see Supporting Information for further details). We could improve this by employing a gain medium with a high refractive index and a small dispersion. This will be the scope of future work.

The dislocations, still present in the self-organized gratings, raise the lasing threshold. We are seeking to further reduce the dislocation density by reformulating the PDMS and by exploring the parameter space of the oxidizing plasma.

In summary, tunable organic lasers that rely on stretchable, self-organized distributed feedback gratings were produced. To prepare the gratings, the surface of a stretched PDMS membrane was hardened by plasma oxidation and then released. The deposition of the organic gain medium from solution exemplifies a laser structure of unsurpassed simplicity of fabrication. In addition, these elastic lasers exhibit a low lasing threshold of 28 μJ cm^{-2} and a continuous wavelength tunability of around 4.7 nm by mechanical stretching. That the devices can be stretched up to 10% is the first insight into creating organic solid state lasers with a tuning range in excess of 20 nm. These results demonstrate the outstanding level of ordering that can be achieved by self-organization. With this class of potentially large-area elastic lasers, novel applications such as strain-sensing optical skins become possible.

Experimental Section

Preparation of Gratings: To fabricate crack-free self-organized gratings of minimized dislocation density, a 1:4 mixture of curing agent and PDMS precursor (Dow Corning Sylgard 184) was spin-coated at 150 rpm on an h_{foil} = 50 μm thick polyimide foil (Kapton E) on top of a glass substrate. The PDMS layer was cured for 24 h at 59 °C. The h_s = 250 μm thick PDMS-on-Kapton sample was removed from the glass, cut in 10-mm-wide stripes, bent around a plastic tube of radius R = 2.3 mm, and fixed with Kapton tape. Given that the elastic modulus of Kapton, E_{foil} = 5.0 GPa, was much higher than that of PDMS, E_s = 2.0 MPa, the neutral plane of the bent PDMS/Kapton stripe was very close to $R + h_{foil}/2$.[32] The resulting prestrain on the PDMS surface at $R + h_{foil} + h_s$ was:

$$\varepsilon_{pre} \approx \frac{h_s + h_{foil}/2}{R + h_{foil}/2} \approx 12\%$$

The mounting tube was placed end-down at the center of a plasma reactor (Supporting Information, Figure 1b). The gratings used for the organic lasers of period $\Lambda = 420$ nm, modulation depth of $2A \approx 50$ nm, and $n_D \approx 1.2 \times 10^4$ mm^{-2} were treated at an oxygen pressure of 30 mTorr, a plasma power of 100 mW cm^{-2}, and a dose of 12 J cm^{-2}. The stripes were flattened immediately after removal from the plasma reactor to release the prestrain and form the grating.

The cast and cure gratings replicated an oxidized silicon wafer master. A self-assembled monolayer of 1H,1H,2H,2H-perfluorooctyltrichlorosilane was applied to the SiO_2 surface for easy PDMS removal.

After casting the mixture of curing agent and PDMS precursor, the sample was first stored in fore-vacuum for about 10 min and then covered with a piece of Kapton foil to level the PDMS surface. After curing, the cast and cure grating was removed from the master by pulling on the Kapton foil. PDMS mix and curing were identical to the self-organized gratings. The PDMS surface was treated with oxygen plasma (30 mTorr, 3 J cm^{-2}) to promote adhesion of the organic emitter. The grating preparation is illustrated in the Supporting Information.

Optical Excitation and Characterization of the Lasers: The third harmonic of a neodymium yttrium vanadate laser AOT (AOT-YVO-25QSPHP/MOPA) at a wavelength of 355 nm, pump pulse width of 700 ps, and repetition rate of 500 Hz was used to pump the organic lasers. The laser output was focused to a spot of approximately 0.038 mm^2. The emission from the sample was dispersed in a Triax 320 monochromator (grating 1200 lines mm^{-1}, Jobin Yvon) and detected by a liquid-nitrogen-cooled charge coupled device camera. The spectral resolution was around 1.8 Å. During all optical measurements the samples were mounted in a dry-nitrogen-purged sample chamber.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

P.G. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship. This research is supported in part by the New Jersey Commission for Brain Injury Research.

Received: August 27, 2010
Revised: November 22, 2010
Published online:

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