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All-polymer organic semiconductor laser chips: Parallel fabrication and encapsulation

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Abstract: Organic semiconductor lasers are of particular interest as tunable visible laser light sources. For bringing those to market encapsulation is needed to ensure practicable lifetimes. Additionally, fabrication technologies suitable for mass production must be used. We introduce all-polymer chips comprising encapsulated distributed feedback organic semiconductor lasers. Several chips are fabricated in parallel by thermal nanoimprint of the feedback grating on 4" wafer scale out of poly(methyl methacrylate) (PMMA) and cyclic olefin copolymer (COC). The lasers consisting of the organic semiconductor tris(8-hydroxyquinoline) aluminum (Alq₃) doped with the laser dye 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyrene (DCM) are hermetically sealed by thermally bonding a polymer lid. The organic thin film is placed in a basin within the substrate and is not in direct contact to the lid. Thus, the spectral properties of the lasers are unmodified in comparison to unencapsulated lasers. Grating periods of 378 nm to 428 nm in steps of 10 nm result in lasing at wavelengths of 622 nm to 685 nm. The operational lifetime of the lasers expressed in number of pulses is improved 11-fold (PMMA) and 3-fold (COC) in comparison to unencapsulated PMMA devices.

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OCIS codes: (140.3490) Lasers, distributed-feedback; (140.7300) Visible lasers; (130.3120) Integrated optics devices.

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1. Introduction

Organic semiconductor distributed feedback (DFB) lasers [1] are of particular interest as tunable emitters of laser light in the visible wavelength range [2]. They are optically pumped, usually by ultraviolet lasers. Low threshold organic semiconductor lasers can be pumped with laser diodes [3–6] and light-emitting diodes [7]. Investigations are also aiming towards electrically pumped lasers [8]. Nevertheless, optically pumped organic semiconductor lasers have sufficient output power for spectroscopic analysis [9–11]. Thus, applications as free space light sources or in integrated photonic systems can be addressed. Particularly, the use in photonic lab-on-a-chip systems will allow for point of care analysis with laser light [12, 13].

Organic semiconductors lack from degradation when exposed to air or water during operation. Thus, encapsulation is needed to ensure practicable lifetimes. Bulović et al. reported on organic semiconductor microcavity lasers encapsulated by evaporated organic and metal layers [14]. Richardson et al. demonstrated encapsulation with an optical adhesive on top of organic semiconductor lasers [15]. Persano et al. presented encapsulation utilizing a rapid prototyping technique and additionally gave an overview over present encapsulation schemes for organic photonic devices [16]. However, these techniques cannot avoid degradation completely. Hence, for bringing organic semiconductor lasers to market low-cost disposable devices are required in order to allow for simple chip replacement after degradation. For such disposable devices optical pumping is advantageous as no electrical elements need to be integrated. Consequently, a reduction of substrate material costs is desired and fabrication technologies suitable for mass production must be used. The combination of thermal nanoimprint and thermal bonding of all-polymer devices is a promising approach to fulfill all of these requirements.

In this paper, we present all-polymer chips out of poly(methyl methacrylate) (PMMA) and cyclic olefin copolymer (COC) comprising several encapsulated organic semiconductor DFB lasers, respectively. The chips are assembled by a few parallel fabrication steps including an organic semiconductor material and PMMA or COC only. Encapsulation is accomplished by thermally bonding a lid of the same polymer, PMMA or COC, respectively.

2. Design and fabrication

For the fabrication of all-polymer organic semiconductor laser chips HesaGlas[®] VOS PMMA [17] and TOPAS[®] 6013 COC [18] were chosen as substrate materials. Both can be structured on the micro- and nanoscale by thermal imprint. Additionally, both polymers are comparably inexpensive and transparent for visible light. For encapsulation their oxygen permeability is crucial which is three times lower for PMMA than for COC [19]. The organic semiconductor tris(8-hydroxyquinoline) aluminum (Alq_3) doped with the laser dye 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyrene (DCM) forms a very efficient Förster energy transfer system and is frequently used for organic semiconductor DFB lasers [20]. The photostability of Alq_3 :DCM is defined by the DCM guest molecules due to the Förster energy transfer. The main contribution to the photodegradation of DCM is due to the interaction of the dye with oxygen [21]. Aiming for top emitting devices we have chosen second order linear DFB gratings. A duty-cycle of ~25% is used which is known to give low thresholds for second order gratings [22].

The main process steps for the fabrication of all-polymer organic semiconductor chips are thermal nanoimprint, evaporation of the organic thin film through a stencil shadow mask, and thermal bonding of a lid (Fig. 1a). The lasers are placed in basins that are closed and thus hermetically encapsulated by the lid. The length and width of the basins is 0.5 mm each. The height of the basins is 1.6 μm . The depth of the DFB gratings is approx. 140 nm and grating periods Λ are varying from 378 nm to 428 nm in steps of 10 nm. A photograph of such all-polymer chips with several integrated lasers having different grating periods is shown in Fig. 1b. Additionally a microscope image of a laser on the PMMA chip illustrates via its contrast and the appearing interference effects that the lid is not in intimate contact with the organic thin film.

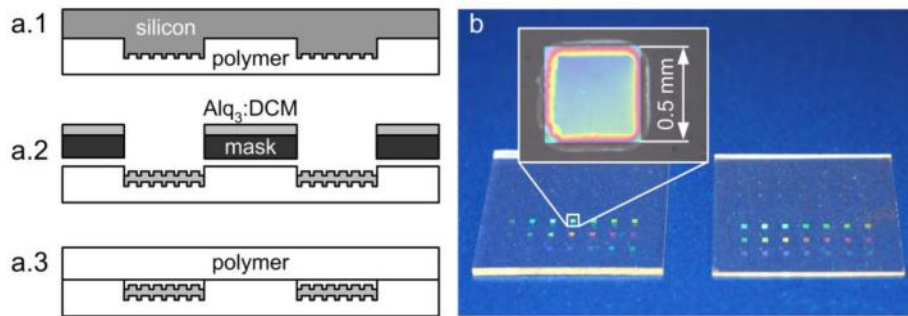


Fig. 1. Scheme of the main fabrication steps of all-polymer chips comprising encapsulated organic semiconductor lasers. (a.1) Thermal nanoimprint. (a.2) Evaporation of Alq_3 :DCM. (a.3) Hermetic sealing by thermal bonding. (b) Photograph of two chips of the size of a microscope cover slip ($18 \times 18 \text{ mm}^2$) with encapsulated lasers and a microscope image of a laser (inset). The lasers can be identified by light diffracted from the nanostructures. The left chip consists of PMMA the right one of COC.

In the following the fabrication process of the all-polymer chips is described in detail. At first, a silicon stamp was fabricated. Its production started with electron beam (e-beam) lithography of the DFB grating pattern. On a 4" silicon wafer ZEP520A resist (Zeon Corporation) was spin coated for 30 s at 2000 rpm and baked on a hotplate at 180 °C for 5 min. The structures were defined using a JEOL e-beam writer at an acceleration voltage of 100 kV, with a dose of 180 $\mu\text{C}/\text{cm}^2$ at a current of 2 nA. On an area of $0.5 \times 0.5 \text{ mm}^2$ each gratings with periods of $\Lambda = 380, 390, 400, 410, 420, 430 \text{ nm}$ were fabricated on the wafer. After development of the resist with ZED-N50 (Zeon Corporation) 30 nm of aluminum were deposited on to the sample by e-beam evaporation. An ultra-sound assisted lift-off resulted in an aluminum grating pattern on the silicon. This metal layer was then used as a mask for etching 140 nm deep gratings into the silicon wafer by SF_6 based reactive ion etching (RIE). Afterwards, the aluminum was removed and AZ[®]5214E resist was spin coated to a thickness

of 1.5 μm and structured by UV lithography, covering the nanostructured area. In another RIE step the silicon was etched down to a depth of 1.6 μm excluding the protected nanostructured area. Thus, the nanostructure is elevated on the stamp and after replication basins comprising the nanostructures for the lasers are generated. Subsequently, the resist is removed and an antistiction coating finishes the stamp.

The stamp was replicated into semifinished HesaGlas[®] VOS PMMA and TOPAS[®] 6013 COC substrates utilizing a Jenoptik HEX 03 hot embossing system, see Fig. 1a. In the case of PMMA the substrate thickness was 0.5 mm. A temperature of 190 °C and a pressure of 2.65 MPa were applied for 15 min. Figure 2 exemplarily shows atomic force micrographs of imprinted PMMA gratings. The stamp was also used for thermal nanoimprint into 0.1 mm thick COC foils at 1.9 MPa and 190 °C for 15 min resulting in gratings of similar quality [23]. Shrinking of the polymer in comparison to the stamp by a factor of 0.995 was experienced after nanoimprinting for both materials.

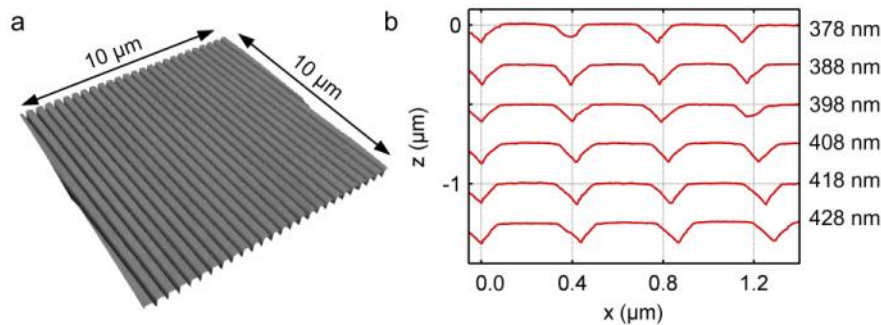


Fig. 2. (a) Exemplary atomic force micrograph of a nanoimprinted DFB grating on a HesaGlas[®] VOS PMMA substrate. The depth of the trenches is 140 nm. (b) Atomic force micrographs of six different PMMA gratings with varying period on one substrate.

Alq₃ and 2.3% by weight of DCM were thermally co-evaporated in a high vacuum chamber up to a thickness of 350 nm onto the different substrates. Using a stencil shadow mask the organic semiconductor was applied on top of the gratings only. Encapsulation was achieved by thermal bonding utilizing the Jenoptik HEX 03 hot embossing system again. Before bonding, the chamber was evacuated down to a pressure of 5 mbar, which is the lowest pressure achievable with this machine. A HesaGlas[®] VOS PMMA lid of 0.5 mm thickness and a TOPAS[®] 6013 COC lid of 0.25 mm thickness were applied on the corresponding substrates. In the case of PMMA, a temperature of 78 C and a pressure of 2.65 MPa were applied for 15 min, still on 4" wafer scale. For COC 0.8 MPa at 110 C for 20 min were used. For nanoimprinting, thin foils are beneficial as the material flow is reduced in comparison to thicker substrates. Thus, a 0.1 mm thick foil as substrate and 0.25 mm thick lid for stability is used in the case of COC. These thicknesses were not available for the PMMA grade used. Finally, a dicing saw was used to separate the PMMA and COC wafers into chips of the size of a microscope cover slip as shown in Fig. 1b.

3. Results and discussion

For characterization the organic semiconductor lasers embedded into the all-polymer chips were excited with an actively Q-switched frequency-tripled neodymium-doped yttrium lithium fluoride laser (Newport Explorer Scientific) emitting pulses of < 5 ns length at 349 nm. The spot diameter of the pump laser on the devices was adjusted to approx. 400 μm . The lasers were pumped from the substrate side in order to allow for comparison of the characteristics of encapsulated and unencapsulated lasers. This also avoids unnecessary losses at the vacuum interfaces, which would occur when pumping encapsulated lasers from the lid side. The pulse energy was controlled with a pulse energy meter (Coherent LabMax-TOP, J-10MT-10 kHz EnergyMax Pyroelectric Sensor). The pump power was monitored during operation using a beam splitter and a calibrated photodiode. With a variable neutral density

filter the pump power was adjusted during operation. The spot position on the chips was controlled with a microscope combined with a charge-coupled device (CCD) camera. Using a microscope objective on the opposite side of the pump beam the light from the organic semiconductor lasers was collected and coupled into a multi-mode optical fiber leading to a fiber-coupled spectrograph (Acton Research SpectraPro 300i, variable grating) connected to an intensified CCD-camera (Princeton Research, PiMax 512).

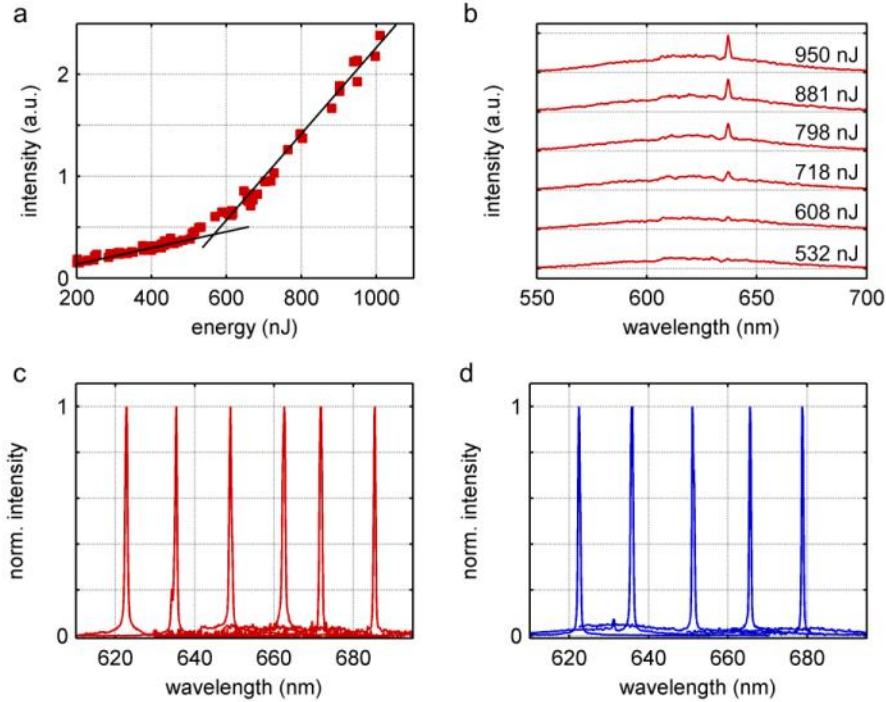


Fig. 3. (a) Input-output curve of an encapsulated PMMA laser and (b) corresponding spectra of the same laser for selected pump energies. (c) Spectra of different lasers pumped well above threshold all integrated on one PMMA chip. Grating periods are 378, 388, 398, 408, 418, and 428 nm. (d) Spectra of lasers on one COC chip for grating periods of 378, 388, 398, 408, and 418 nm.

Figure 3a shows the input-output curve of a DFB laser on PMMA with a grating period of $\Lambda = 388$ nm. Corresponding spectra are plotted in Fig. 3b showing that the lasing threshold of this laser is approx. $0.6 \mu\text{J}$. Figures 3c,d show spectra of different PMMA and COC lasers with grating periods corresponding to the gratings shown in Fig. 2b. The emitted laser light is TE polarized. The thresholds of these lasers are plotted in Fig. 4a as solid symbols. However, the solid plotted pulse energies are not the actual pulse energies that reach the gain material. Both PMMA and COC absorb the pump beam partially. The absorption is 94% for PMMA substrates and 1% for COC substrates at the wavelength of the pump laser of 349 nm as measured using a photospectrometer (Perkin Elmer, Lambda 1050). Using the data obtained from the absorption curve reveals that the lowest threshold for the PMMA laser is approx. 36 nJ and approx. $0.4 \mu\text{J}$ for the COC lasers. The corrected threshold energies are plotted in Fig. 4a as well. The thresholds of the PMMA lasers are much lower than the thresholds of the COC lasers. In contrast to this, the thresholds were comparable for unencapsulated lasers for both materials if pumped from the Alq_3 :DCM side. The disagreement may be assigned to the fact that the COC lasers were heated up to 110°C during bonding which can lead to thermal degradation of the active material. This temperature is close to the temperature used for the thermal evaporation of DCM of $\sim 120^\circ\text{C}$.

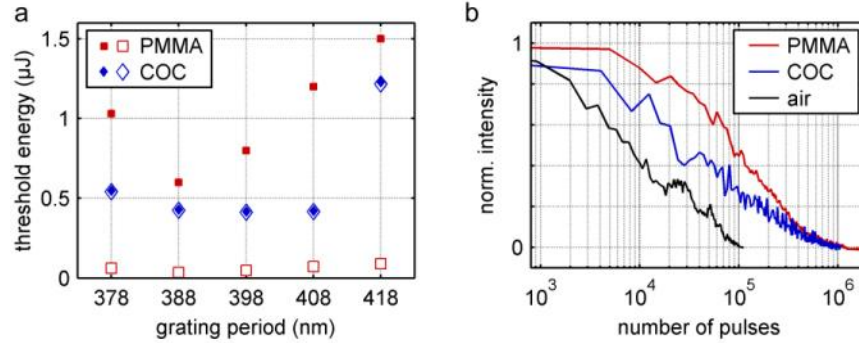


Fig. 4. (a) Threshold of PMMA and COC lasers for grating periods from 378 nm to 418 nm. The device thresholds are plotted with solid symbols. As the polymer material absorbs the pump light partially estimated laser thresholds are plotted using open symbols. (b) Lifetime measurements of an encapsulated PMMA laser and an encapsulated COC laser in comparison to an unencapsulated laser.

The lifetime of the encapsulated lasers was investigated by pumping them with approx. eleven times their threshold energy with a constant pulse repetition rate of 1 kHz. An unencapsulated PMMA device was investigated in a similar manner. A spectrum was taken every 100 pulses in the case of the unencapsulated device and every 4000 and 5000 pulses for the encapsulated PMMA and COC devices respectively. In Fig. 4b, the intensity at the spectral emission maximum of three typical lasers is plotted as function of the number of pulses. For this plot, the final intensity after lasing activity has ceased was subtracted from the measured intensity to disregard photoluminescence in the lifetime measurement. Finally, these values were normalized for better comparison of the lasers. In the case of an unencapsulated laser operated in air, the intensity dropped to 50% of the initial value after $0.8 \cdot 10^4$ pulses. For the encapsulated devices this occurred after $2.3 \cdot 10^4$ pulses for COC and $8.4 \cdot 10^4$ pulses for PMMA. Thus, the lifetime of the laser expressed in number of pulses is enhanced approx. 3-fold for COC and 11-fold for PMMA. The degradation can be attributed to the presence of little oxygen inside the small cavity on top of the lasers. The accumulated pump energy that hit the organic lasers until their output energy dropped to the half of its initial value was 1.88 J/cm^2 for the encapsulated PMMA laser (absorption corrected), 6.18 J/cm^2 for the encapsulated COC laser, and 0.18 J/cm^2 for the unencapsulated laser (absorption corrected). The pump spot diameter was $\sim 400 \mu\text{m}$ in each case. According to these results, the lifetime expressed in absorbed energy increases approx. 34-fold for COC and 10-fold for PMMA. After this experiment, lasing could be observed as soon as the pump energy was increased for all the devices. As in the case of epoxy encapsulation [15] a blue-shift in the emission wavelength occurs during operation. The wavelength change was $\sim 0.02 \text{ nm}/10^5$ pulses for the PMMA laser and $\sim 5.2 \text{ nm}/10^5$ pulses for the COC lasers. For the unencapsulated PMMA device a shift of $\sim 2.6 \text{ nm}/10^4$ pulses was measured. The overall efficiency before degradation of the encapsulated PMMA devices is $\sim 1\%$ (the absorption is again corrected) and $\sim 0.7\%$ for encapsulated COC devices. Organic semiconductor microcavity lasers have a nearly temperature independent performance for temperatures from 0 - 140 °C in vacuum [24]. Due to the presence of little oxygen in our devices, an enhanced degradation can be expected with increasing temperature.

4. Summary and conclusions

Encapsulation of organic semiconductor lasers is necessary to ensure practicable lifetimes for spectroscopic applications. The use of parallel wafer scale processes which are transferable to mass production is also essential to bring organic semiconductor lasers to market.

Here, we demonstrated organic semiconductor DFB lasers hermetically vacuum-sealed into HesaGlas[®] VOS PMMA and TOPAS[®] 6013 COC chips. The all-polymer chips are fabricated on 4" wafer scale using thermal nanoimprint and bonding. Lasing is shown for

different grating periods resulting in wavelengths from 623 nm to 685 nm. An 11-fold (PMMA) and 3-fold (COC) enhanced lifetime expressed in number of pulses of the encapsulated lasers in comparison to similar unencapsulated devices is shown. As the encapsulating lid does not get into direct contact, the organic thin film is not affected and the spectral properties of the lasers are not modified. Thinner PMMA substrates or specific PMMA that does not absorb the pump light (e.g. available from Topacryl AG) could decrease the PMMA device threshold. The presented all-polymer chips can be used as free space light source in combination with an appropriate pump source. Integrating the lasers into lab-on-chip photonic microsystems will allow for attenuation measurements, excitation of fluorescent markers, and spectroscopic applications.

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