Fabrication of Circular Grating Distributed Feedback Dye Laser by Nanoimprint Lithography

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1. Introduction

Within recent years the development of polymer dye lasers has progressed to higher levels of performance and functionality. The most attractive advantages of polymer dye lasers include low-cost processing, wide choice of emission wavelengths, and easy fabrication on flexible substrates. Several waveguide dye lasers have been studied with emission wavelengths ranging from ultraviolet to near infrared (Y. Oki et al., 2002). By simply changing the fluorophore doped in the polymer, these lasers can be used as the tunable sources for various applications, such as spectroscopy (Y. Oki et al., 2002) and fluorescence excitation source (C. Vannahme, 2011). Furthermore, microlaser array with multiwavelength emissions can be achieved (Y. Huang et al., 2010) for more applications such as compact displays and multiwavelength biosensors.

Currently the integration of miniaturized active light sources such as lasers into microfluidic systems becomes an attractive approach for biological and chemical processes (D. Psaltis et al., 2006). A majority of microfluidic systems are based on external light sources. However, the coupling of optical signals in and out of the devices, typically by optical fibers, remains one of the major challenges in integrated optics. By making on-chip light sources, we can eliminate the optics alignment, which greatly reduces the complexity of the system (E. Verpoorte, 2003). For applications in biochemical analysis in microfluidic systems, a surface emitting laser would appear to be more useful than other lasers because of its stacked substrate structure. Therefore, we choose a circular grating structure as the laser resonator design to produce low-threshold surface emitting lasing. The laser operating characteristics can be significantly improved by the two-dimensional nature of the resonator structure, and they are suitable to serve as low-threshold, surface-emitting coherent light source in microfluidic networks.

The 1-D distributed feedback (DFB) structure is a widely employed resonator geometry, and has been previously demonstrated for polymer lasers (Y. Oki et al., 2002). However, operating characteristics can be significantly improved within 2-D structures. Here, we choose a circular grating distributed feedback structure to obtain low threshold operation, a well-defined output beam, and vertical emission perpendicular to the device plane.
Although surface emitting circular grating lasers using semiconducting polymers have been previously demonstrated (Bauer et al., 2001; Turnbull et al., 2005), their lasers were fabricated by depositing the organic gain material onto prepatterned dielectric substrates, limiting the depth and the accuracy of the shape of the grating.

For better geometric control, we choose nanoimprint lithography (S. Y. Chou et al., 1996) as a direct patterning method. Nanoimprint lithography is the technique that can effectively produce nano pattern with line width below 100nm. In general, a hard mold is used to transfer patterns with high fidelity into target polymers, and this technique has become an attractive approach to define nanofabricated optical resonator structures. Conjugated polymer lasers fabricated by hot embossing have been studied (J. R. Lawrence et al., 2002), and 1-D DFB lasers based on organic oligomers using a room temperature nanoimprint method were reported (D. Pisignano et al., 2003, 2004).

The basic idea of nanoimprint lithography is to press a mold with nanostructures on its surface into a thin layer of resist on a substrate, followed by the removal of the mold. Nanoimprint is a low cost nanopatterning technology based on the mechanical deformation of a resist, and it is a high-throughput alternative to traditional serial nanolithography technologies.

The imprint step creates a thickness contrast and duplicates the nanostructures in the resist film. During the imprint process, the resist is heated to a temperature above its glass transition temperature. At this temperature, the resist, which is thermoplastic, becomes a viscous liquid and can be deformed into the shape of the mold. Therefore, this method allows the nanostructure on the mold to be faithfully transferred to the polymer substrate.

The well developed nanoimprint technology provides a convenient way of mass production and large-scale fabrication of low-cost dye laser arrays with a wide wavelength output range. It is also straightforward to build on-chip dye lasers with waveguides to replace the optical fibers necessary for the integrated optics. The miniaturized dye lasers can serve as surface emitting coherent light sources, which are very important in various biochemical applications, such as laser-induced fluorescence and spectroscopy.

In this chapter, we report the fabrication of a circular grating distributed feedback laser on dye-doped poly(methylmethacrylate) (PMMA) films (Y. Chen et al., 2007). The schematic diagram of a nanoimprinted circular grating dye laser chip is illustrated in Figure 1. The laser was fabricated on a glass substrate using a low-cost and manufacturable nanoimprint method. In this solid-state dye laser device, the laser dye is doped in the polymer forming the laser resonator, which can produce high-intensity and narrow-linewidth lasing with a well-defined output beam. With certain selected grating period, surface emission lasing with single frequency at 618 nm and a linewidth of 0.18 nm was measured from the polymer dye laser exhibiting a threshold value of 1.31 μJ/mm². The laser operation characteristics of the circular grating resonator are improved through the high accuracy and aspect ratio nanoimprint pattern transfer. Moreover, the mold can be re-used repeatedly, providing a convenient way of mass production and large-scale fabrication of low-cost polymer dye laser arrays. The on-chip dye lasers allow the integration of coherent light sources with other microfluidic and optical functionalities, and provide possibilities for building more complete “lab-on-a-chip” systems.
2. Laser cavity design

Laser (Light Amplification by Stimulated Emission of Radiation) is composed of a gain medium and a resonant optical cavity (A. E. Siegman, 1986; F.P.Schafer, 1990). The gain medium amplifies the beam by stimulated emission, and the resonant cavity provides the feedback necessary for the lasing operation. For our solid-state dye lasers, we choose the circular grating resonator as laser cavities for their unique two-dimensional nature and enhanced lasing performance.

The circular grating structure proposed (T. Erdogan, 1990) and demonstrated (T. Erdogan, 1992) by Erdogan provides a natural 2-D extension of the basic DFB structure. It allows feedback to be applied in all in-plane directions, and the second-order grating couples the emitted radiation perpendicularly out of the surface of the sample. Figure 2 shows a general design of a circular grating distributed feedback structure. A theoretical analysis of circular grating lasers is described in detail elsewhere (C. M. Wu et al., 1991; T. Erdogan et al., 1992; P. L. Greene et al., 2001; G. F. Barlow et al., 2004; G. A. Turnbull et al., 2005) predicting that only the radial propagating components define the modes in the circularly symmetric grating.

The distributed feedback scheme indicates that the gain material is directly implemented in the grating structure. The circular grating DFB structure satisfies the second-order Bragg condition, \( \lambda_{\text{Bragg}} = n_{\text{eff}} \Lambda \), where \( \lambda_{\text{Bragg}} \) is the emission wavelength, \( n_{\text{eff}} \) is the effective index of the waveguide mode, and \( \Lambda \) is the grating period, with an inner cavity providing a quarter- or half-wavelength shift similar to the classical DFB case.

The second-order grating is used to obtain surface emission, because it not only couples counter-propagating radial waves (via second-order Bragg reflection), but also induces coupling of radially propagating waves into the direction normal to the grating surface (via first-order Bragg reflection). The corrugations in the grating structure provide both distributed feedback and output coupling of the guided optical mode via second-order and first-order Bragg scattering.
For the theoretical analysis of the grating structure, we use a transfer matrix method appropriate for description of the optical modes of circular grating microcavities. The electromagnetic modes of cylindrical multilayer structures are analyzed in terms of propagating waves, i.e., Hankel functions (A. Yariv, 1997; D. Ochoa et al., 2000). Using the transfer matrix method based 2-D cylindrical model, the spectrum information of the cavity modes can be obtained to analyze the energy confinement in the circular grating structure (A. Jebali et al. 2007).

The design parameters of the circular gratings fabricated are selected based on electromagnetic mode calculations and experimental results. A grating period of 440 nm is chosen to match the second-order Bragg condition. The center defect is a 440 nm diameter gain region. The 400 nm groove depth is defined to ensure maximum confinement, whereas the 200 µm overall diameter of the circular grating and the 50% duty cycle are used to reach the maximum coupling strength (A. Jebali et al., 2004).

3. Method of device fabrication

3.1 Materials

The materials used in the solid state dye laser chip are chosen for three layers of the device: the substrate, the cladding, and the polymer matrix. The substrate for the solid-state dye laser could be Silicon or Silicon dioxide, while the cladding material is Cytop, and the gain medium is dye doped PMMA.

The PMMA (poly(methylmethacrylate)) is a well-known highly transparent thermoplastic. In our laser device, we chose PMMA to be the dye host matrix as well as the nanoimprint material. PMMA was selected as the polymer matrix because of its solubility of the dye molecules, as well as its low absorption at the wavelength for activating the dye molecule. Using PMMA in nanoimprint lithography is very common due to its small shrinkage under large changes of temperature and pressure (S. Y. Chou, et al., 1995). The mold release property of PMMA can be improved by spray coating a release agent on its surface (M. Okada, et al., 2009).

The organic laser dye we use in the laser device is Rhodamine 640 (Exciton). This laser dye has excellent stability for its large quantum efficiency and relatively long life time before
bleaching. We chose Rhodamine 640 to match its absorption peak with the cavity resonant frequency. To dope the organic dye molecules into the polymer, we mixed PMMA with chlorobenzene, methyl isobutyl ketone, ethanol, and Rhodamine 640 to make a 30 mM solution.

Cytop is a low refractive index perfluoropolymer with special molecular structure. This cyclic fluoro-polymer, poly(1,1,2,4,4,5,6,7,7-decafluoro-3-oxa-1,6-heptadiene) is made by Asahi chemicals and used in the electronics industry. It is a hard but amorphous material with Tg ~ 108 °C. We chose Cytop as a cladding material because of its low refractive index (n=1.34). The material system of PMMA and Cytop has previously been used for commercial polymer optical fibers and simple waveguides (Y. G. Zhao et al., 2000), and using Cytop-PMMA as polymer waveguides for sensing has also been reported (B. Agnarsson et al., 2010).

3.2 Mold fabrication

The mold fabrication process is essential, it defines the laser resonator geometry, and the shape of the mold structure and surface roughness will eventually affect the laser device performance. In our experiments, silicon dioxide (SiO$_2$) was used as the mold material. The grating pattern was defined by electron beam lithography on a LEICA EBPG 5000+ e-beam writer. 8% 495K PMMA was spun on a SiO$_2$ substrate and baked for 15 min at 170 °C, which formed a 400 nm thick resist layer. The PMMA was exposed by electron beam with proximity correction. Development of patterned PMMA film was carried out in a 1:3 MIBK:IPA (methyl isobutyl ketone and isopropanol alcohol) solution for 1 min. The pattern was subsequently transferred from PMMA into SiO$_2$ substrate via reactive ion etching (RIE) using fluorine chemistry (CHF$_3$). The condition of RIE was 20 sccm, 60 mTorr of CHF$_3$ at 110 W for 15 min. Finally the PMMA residue was removed by sonicating the wafer in Chloroform for 2 min. The SiO$_2$ etching rate in the CHF$_3$ RIE process is 30 to 35 nm per min.

The SEM images of both the top view and the angled view of an etched SiO$_2$ mold of circular grating are shown in Figure 3. In this particular mold, the grating period is 440 nm, with a center defect of 440 nm and an overall diameter of 200 µm, and the trench depth is 400 nm.

**Fig. 3.** The SEM images of the top view and the angled view of SiO2 mold
3.3 Laser chip fabrication

The laser chip consists of three layers, the substrate, the cladding, and the polymer matrix. PMMA was selected as the polymer matrix because of the solubility of the dye in PMMA, as well as its low optical absorption within the wavelength range for activating the dye molecules, and its excellent properties for nanoimprint lithography.

To construct the dye laser, a glass substrate (SiO$_2$) was spin-coated with Cytop, a low-refractive-index material (n=1.34) as the lower cladding to ensure the vertical optical confinement. After an oxygen plasma treatment to improve the adhesion of Cytop to the PMMA, dye-doped PMMA (n=1.49) was spun on top of the Cytop layer to serve as the gain medium.

The Cytop and PMMA preparation process for the nanoimprint process is summarized in Figure 4. We began the fabrication process by depositing a 5 µm thick layer of Cytop (CTL-809M, Asahi Glass) on a silicon dioxide substrate. The deposition of the Cytop was accomplished via a series of spinning and thermal curing steps to ensure flatness and uniformity over the wafer.

First, we spun the Cytop on the substrate at 1500 rpm (adhesion promoters were not necessary). Next, the Cytop was baked at 65 °C for 60 s, 95 °C for 60 s, and 180 °C for 20 min. The ramping of the bake temperature was critical in attaining flat and uniform surfaces. The spinning and baking steps were then repeated two more times, with a final bake at 180 °C for 3 hours. After the chip cooled down, an oxygen plasma treatment (Anatech SP100) of the Cytop was necessary for the adhesion of Cytop to PMMA. We exposed the oxygen plasma to Cytop at an RF power of 80 W and O$_2$ pressure of 200 mTorr for 30 s.

Next, dye (Rhodamine 640, Exciton)-doped PMMA (30 mM) was spin-coated on top of the Cytop layer at 500 rpm for 15 s and then 5000 rpm for 1 min. This produced a dye-doped polymer thin film with 600 nm thickness as the gain medium. A prebake at 170 °C for 2 min before the nanoimprint process ensured solvents were evaporated and improved the adhesion between the Cytop and PMMA. Then the substrate was ready for the nanoimprint process to define the laser cavity structure.

![Fig. 4. The schematic procedure of the Cytop and PMMA substrate preparation process](www.intechopen.com)
3.4 Nanoimprint process

Nanoimprint lithography exploits the glass transition of polymers to achieve high-fidelity pattern transfer. However, degradation of the light emission efficiency of the organic materials during air exposure at high temperatures presents a challenge in nanoimprint lithography (J. Wang et al., 1999). To solve this problem, a modified nanoimprint method is used to prevent this degradation of the dye-doped PMMA film by sealing the mold and the PMMA substrate into a curable polymer during the imprinting process.

During the nanoimprint process, a mold release reagent such as 1H,1H,2H,2H-perfluorodecyl-trichlorosilane (Alfa Aesar) was also deposited on the dye from the vapor phase to reduce the resist adhesion to the mold. Then, the mold was pressed into the PMMA film by using an automatic mounting press machine (Buehler SimpliMet 1000) at a temperature of 150 °C (above PMMA’s glass transition temperature) and a pressure of 1200 psi. After sample cooling, the mold could be easily separated from the patterned polymer laser chip. The nanoimprint process is schematized in Figure 5.

![Nanoimprint process diagram](image)

Fig. 5. The schematic nanoimprint process of circular grating polymer dye laser

Figure 6 shows the SEM images of the mold and the imprinted PMMA. From these pictures, we can observe that the structure on the SiO₂ mold is faithfully replicated on the PMMA substrate surface with high resolution. Photoluminescence spectra confirm that there is no degradation of the luminescence performance of the polymer. Compared to various methods of defining nanostructures such as Extreme UV and E-beam lithography, the modified nanoimprint lithography is a suitable method for fabricating dye laser resonator structures, since it will not cause the degradation of fluorophores doped in the polymer
matrix. Also nanoimprint lithography is considered a low cost fabrication technique, enabling the mass production of dye laser array devices using a single master mold.

Fig. 6. SEM images of (a) the SiO$_2$ mold and (b) the imprinted PMMA film.

4. Results and discussion

The measurement setup of the polymer dye laser chip is shown in Figure 7. The polymer laser chip was optically pumped with 6 ns Q-switched Nd:YAG laser pulses at 532 nm wavelength, focused through a 20X objective to the top side of the chip. A 10X microscope objective was used to collect the emission from the bottom side of the chip and deliver it to a fiber coupled CCD-array-based spectrometer with 0.1 nm resolution (Ocean Optics HR4000).

Fig. 7. The measurement setup of polymer dye lasers
A typical single-frequency lasing spectrum of the dye laser chip is shown in Figure 8. The lasing wavelength is 618.52 nm, and the measured linewidth is 0.18 nm. Lasing occurs near the Bragg resonance, determined by the equation $m\lambda_{\text{Bragg}} = 2n_{\text{eff}}\Lambda$, where $m = 2$ is the order of diffraction, $n_{\text{eff}}$ is the effective refractive index of the propagation mode, and $\Lambda$ is the grating period. The linewidth near threshold is measured as 0.20 nm, which results in a cavity quality factor (Q) of over 3000. The measured lasing from the solid-state dye laser shows that a high intensity, narrow linewidth, well-defined output beam is achieved by the circular grating resonator. Different lasing wavelength output can be obtained by changing the dye molecule doped in the polymer or varying the period of the grating structure.

![Graph](image)

Fig. 8. Nanoimprinted circular grating DFB dye laser spectrum. The measured linewidth is 0.18 nm. Inset: Polymer laser chip excited by Nd:YAG 532 nm laser pulse.

Figure 9 shows the variation of the output laser power as a function of absorbed pump energy. With the absorbed threshold energy of 41.3 nJ, the threshold pump fluence is estimated to be 1.31 µJ/mm². This pump intensity is well within the reach of commercial high power blue laser diodes, enabling a self-contained Laser diode pumped device. The polymer laser is pumped from the surface of the chip and the lasing emission is collected from the back side of the chip. The transparency of the substrate, the size and geometry of the laser cavity, and the low threshold match well with the output beams of high power LEDs and Laser diodes. Therefore the replication-molded circular grating geometry represents a very promising structure for the construction of compact LED or Laser diode pumped portable dye lasers.
Fig. 9. The output laser power vs. the absorbed pump energy curve. The threshold pump fluence is 1.31 $\mu$J/mm$^2$.

Figure 10 (a) represents the far-field image of the emission pattern recorded by a CCD camera, and Figure 10 (b) shows the far-field radiation patterns of the laser passing through a linear polarizer with different orientation angles. The laser is expected to be azimuthally polarized (R. H. Jordan et al., 1997), as illustrated in the polarization patterns. The azimuthal polarization also results in a zero electrical field (a dark spot) at the center of the laser (T. Erdogan et al., 1992). The Polarization studies of circularly symmetric beams verified theoretical predictions that these beams are azimuthally polarized. In the lasing process, many spatial modes can be excited with their mode thresholds very close to each other (T. Erdogan et al., 1992). The fundamental mode is normally the favored one, because higher order modes do not overlap well with the gain region.

We observe decreases in the laser emission with increasing exposure time. This result is consistent with previous studies on polymer DFB structures (G. Heliotis et al, 2004). The lifetime of polymer dye laser can last over $10^6$ shots of pump laser pulse, and if the characterization of the laser device is carried out under vacuum to inhibit photo-oxidation, the lifetime can be further extended (P. Del Carro et al., 2006). Because of the low cost of materials and fabrication, replication molded devices are disposable and may not require a long lifetime. With the mass production capability, nanoimprinted solid-state dye lasers are suitable for disposable light sources for integration in microsystems.

The integration of solid-state dye laser with microfluidic platform is important. Because of its stacked substrate structure, the alignment of surface emitting dye lasers with microfluidic channels would be straightforward. Since optofluidic dye lasers also have great advantages in microfluidics integration, many on-chip liquid dye lasers with distributed feedback structure have been demonstrated (Z. Y. Li et al., 2006; M. Gersborg-Hansen and A. Kristensen, 2006; S. Balslev and A. Kristensen, 2005) by soft lithography (Y. N. Xia and G. M. Whitesides, 1998).
Fig. 10. (a) Far-field image of the emission pattern recorded by a CCD camera. (b) Circular grating DFB laser far-field radiation patterns through a linear polarizer with different orientation angles. The laser emits an azimuthally polarized, well-confined circular beam.

There are many unique properties of the miniaturized liquid dye lasers in microfluidic systems, the mixing and circulating capabilities enable various ways to tune the laser wavelength (J. C. Galas et al., 2005; Z. Y. Li et al., 2006; M. Gersborg-Hansen and A. Kristensen, 2007). Based on this idea, we can make an optofluidic version of the circular grating dye laser, in which the laser dye is dissolved in an organic solvent and flowed through a microfluidic channel with laser resonator embedded (Y. Chen et al., 2009). The flexibility and versatility of microfluidic fabrication enables the large-scale integration of laser arrays in compact devices with more functionality, which allows us to constantly change the dye to increase the device lifetime and to tune the wavelength.

There are still several issues with the current scheme of the solid-state dye laser. Its relatively high excitation power requires a pulsed Nd:YAG laser as the pumping source, and the reduction of pumping threshold is a very challenging problem. Recent studies show that if the cavity length can be reduced to the order of several micrometers, the optical pumping by a low-power light source, such as a laser diode, can be realized (H. Sakata, and H. Takeuchi, 2008; Y. Yang et al., 2008). The lifetime of the device can also be largely increased by optimizing the organic component of the polymer and reducing the lasing threshold. For the structure of the laser device, surface roughness will greatly affect the quality factor and lasing performance. Further improvements of the anti-adhesive properties of the stamp and the optimization of etching parameters will contribute to future devices.

5. Conclusion

In summary, we have described the fabrication of a surface emitting polymer dye laser with circular grating distributed feedback structure using nanoimprint lithography. We have
achieved excitation thresholds as low as 1.31 μJ/mm² and FWHM linewidths of 0.18 nm. The technique described here enables the fabrication of low cost, high quality and mass producible laser arrays, which may be deployed as compact and inexpensive coherent light sources for lab-on-a-chip applications such as sensing and spectroscopy.

Future work will be focused on improving the laser cavity quality factor (Q) values with better electromagnetic design, optimizing the dye concentration, and fabricating smoother surfaces. One of the future research directions is to use novel soft lithography technique to develop optofluidic dye lasers based on circular grating geometry, in order to realize dye solution circulating and wavelength tuning. Another direction is to use conductive polymer as the gain medium to enable electrically pumped laser scheme. The ultimate goal is to reduce the lasing threshold to enable the use of LEDs or laser diodes as integrated and inexpensive pump sources for on-chip polymer lasers, and integrate the laser chip into microfluidics for further development of complete “lab-on-a-chip” systems.

6. Acknowledgment

This work is supported by the Caltech DARPA Center for Optofluidic Integration under Contract No. HR0011-04-1-0032 and by the Boeing Corporation.

7. References


Nanotechnology has experienced a rapid growth in the past decade, largely owing to the rapid advances in nanofabrication techniques employed to fabricate nano-devices. Nanofabrication can be divided into two categories: "bottom up" approach using chemical synthesis or self assembly, and "top down" approach using nanolithography, thin film deposition and etching techniques. Both topics are covered, though with a focus on the second category. This book contains twenty nine chapters and aims to provide the fundamentals and recent advances of nanofabrication techniques, as well as its device applications. Most chapters focus on in-depth studies of a particular research field, and are thus targeted for researchers, though some chapters focus on the basics of lithographic techniques accessible for upper year undergraduate students. Divided into five parts, this book covers electron beam, focused ion beam, nanoimprint, deep and extreme UV, X-ray, scanning probe, interference, two-photon, and nanosphere lithography.

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