

Fabrication of micro- and nano-phonic structures in dye-doped polymers and nonlinear optical crystals using high energy proton beam

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ABSTRACT

Proton beam writing (PBW) is a new direct-write technique developed at Centre for Ion Beam Applications, National University of Singapore for creating three-dimensional, high aspect ratio micro- and nano-structures with straight and smooth sidewalls in resists, polymers, glasses, and other materials. Here we present some results of our initial efforts on the direct writing of photonic structures in nonlinear optical polymers and crystals. We also present some proposals on the imprinting of waveguides in nonlinear polymers using the high-quality metallic stamps obtained with PBW. The advantages of p-beam writing technique compared to others are discussed.

Keywords: High-energy proton beam, Nonlinear polymer, Nonlinear optical crystal, Nanoimprinting, Waveguides, metallic stamp

1. INTRODUCTION

In optical communications photons (light) carry information from one user to another and devices such as waveguides, splitters, couplers, multiplexers, amplifiers, etc. are essential to maneuver these photons. Such devices can be realized with polymers and/or inorganic materials and integration of all these devices onto one planar substrate is defined as integrated optics [1-3]. The ever increasing demand for higher bandwidth in telecommunications has been one of the driving forces for development of new integrated optoelectronic devices in the last decade. In this context, polymer based materials are of immense interest in integrated optics since they can be easily tailored to meet specific requirements for a variety of applications [4-6]. The significance of high transparency, low cost, rapid processing by direct patterning combined with potential of mass production attracts interest from both scientific and industrial view point. Waveguides in polymers can be designed with very large or very small refractive index contrast between core and cladding (ranging from 0 to 35%). Present polymer technology is capable of manufacturing stress-free layers regardless of the substrate (silicon, glass, quartz, plastic, etc.) combined with low values of birefringence. Polymer waveguides with ultra low optical losses (<0.07 dB/cm) in the telecommunications band (1500-1550 nm) have been demonstrated recently [7]. However, there a few problems like thermal instability associated with polymer based devices. Some of the active devices already demonstrated using polymers include lasers, amplifiers, polarizing elements, filters, modulators, detectors, switches, and attenuators [8-17]. The field of polymer integrated optics is still in its infancy and an iterative approach of design, synthesis, processing, fabrication, and characterization of polymer-based materials is a pre-requisite for development of advanced polymer-based photonic technology platforms.

1(a) PROTON BEAM WRITING & NANOIMPRINTING

Photolithography, e-beam lithography, X-ray lithography are some of the successful techniques over the recent years implemented for fabricating micro-and nano-structures useful for a variety of applications. Photolithography is the selective process that allows the patterning of a desired design onto the material. Photo resist is applied as the first step in applying a pattern in a uniform film. The mask is a metal sheet that holds the actual pattern that will be etched into the photo resist. The mask is cut so that when a UV light is illuminated from behind the exposed parts of the photo resist will be the actual pattern. These exposed parts can then be removed away

(positive resist) or will stay on to the fabricated device (negative resist). Present commercial optical lithography is capable of mass-replicating nanostructures with ~130 nm resolution and is fast approaching its limit set by diffraction (~110 nm for UV light for wavelength of $\lambda=193$ nm) [18]. In order to manufacture devices in the sub-100 nm regime of “post-optical” era, alternative technologies will have to be developed to a position where they are suitable for mass-production [19-21]. Several potential technologies which exist at present include electron-projection, extreme-ultraviolet, and X-ray lithography. Electron beam lithography (EBL) is a serial patterning technique which patterns an electron sensitive polymer. Both negative and positive electron sensitive polymers are commercially available. PMMA, which is a positive resist, is one of the common resists used in EBL and line widths of ~10 nm have been achieved recently. Similar to the case of UVL the resist is developed subsequently to the electron exposure. Extreme Ultraviolet Lithography offers a wavelength of 13 nm, which is ten times shorter than today's best optical alternatives, and will enable the patterning of chip features smaller than 50 nm. Because the wavelength of EUVL is 13 nm, the components required for lithography must be fabricated to sub-nm tolerances. However, the cost and progress of these systems may prevent their immediate utilization. Therefore, a lot of current research efforts are now directed towards the development of alternative cost-effective, high-throughput, high-resolution lithographic techniques for both industrial applications and fundamental studies. Among these approaches, nanoimprint lithography (NIL) is one of the most promising schemes for large-area (even up to 8 inch wafers) mass-replications [22-29]. NIL is similar to photolithography or electron beam lithography, except that a mechanical stamp or mold is used to create the pattern in a resist or a polymer. 'Nanoimprinting' refers to the first step of pressing the pattern in the resist (i.e. embossing), while 'lithography' indicates that a patterned resist is involved in the fabrication process. It has been established that nanoimprinting technique is capable of replicating large-area nanostructures with feature size smaller than 10 nm and the imprint time of approximately a few seconds. The ITRS road map [18] requirement of mass replication of sub-100 nm structures will be successful with a technique capable of producing high-quality stamps in conjunction with NIL.

Proton beam writing (PBW) is a direct-write technique developed recently, and pioneered at National University of Singapore, for creating three-dimensional, high aspect ratio micro- and nano-structures with straight and smooth sidewalls [30-36]. This technique is useful particularly in fabricating arbitrary shape waveguide patterns (e.g. Y-branch, Mach-Zehnder Interferometer, Ring Resonator, and Directional Coupler) and micro-/nano-fluidic channels in different materials like polymers, fused silica, and quartz. We have successfully demonstrated the fabrication of SU-8 channel waveguides and Y-branches [37, 38], PMMA buried channel waveguides [39] and erbium doped IOG-1 waveguide amplifiers [40]. Unlike other techniques, there is no involvement of mask indicating that rapid prototyping of smooth three dimensional structures is an additional advantage. One of the significant achievements of PBW has been fabrication of sub-100 nm structures with almost 90° perpendicular side walls with very low roughness along with metallic replication of those structures [41]. Proton beam machining, with its capability of producing high quality metallic stamps, in combination with NIL has the promise/potential for fulfilling the requirements of future generation lithographies mentioned in the ITRS 2003 roadmap [18]. Unlike in electron beam lithography the proximity effects with protons are minimal leading to better spatial resolution.

1(b) NONLINEAR OPTICAL POLYMERS

Polymers doped with nonlinear materials (eg. Rhodamine, Disperse Red) have been successfully studied for their applications in electro-optic modulation, all-optical switching, and storage devices [42-44]. Doped polymers also find applications in photonic crystals and micro-lasers. Nilsson et al. fabricated micro fluidic Rh 6G dye laser in PMMA using NIL. In the present study we doped PMMA (high molecular weight of 950 K as well as low molecular weights of 120 K and 350 K) with Rhodamine B (RhB), Rhodamine 6G ClO₄ (R6G), Disperse Red, and utilizing NIL we intend to make photonic structures like waveguides and gratings. Alternatively, we could also fabricate buried waveguides in these polymers by direct write technique using high-energy proton beam or ridge waveguides by selective irradiation and development. Here we present some of our initial results on the fabrication and optical characterization of different structures in pure and doped polymers using proton beam writing and NIL.

PMMA acts as a positive resist with irradiation of high energy proton beam. PMMA exposed to high energy protons results in chain scissioning of the polymer. The resulting damaged resist consisting of molecular chains with lower molecular weight is then selectively removed using a suitable chemical developer at room temperature. On the other hand SU-8, a chemically amplified, epoxy based resist crosslinks under proton beam exposure. A suitable chemical developer can then be employed to selectively remove the unexposed areas, indicating

SU-8 a negative resist with proton beam exposure. We approached the fabrication of waveguides in dye doped polymers in two different ways. In the first case we use the proton beam to direct write the waveguides as already been demonstrated in the case of pristine PMMA. Energetic ions passing through polymer material deposit energy mainly due to electronic stopping. Depending on the energy and dose, PMMA undergoes chain scission [18]. The changes in the chemical and physical structure of the polymer lead to the compaction and densification of the material, leading to increase in the refractive index. The largest change of refractive index occurs near the end of range (~ 62 mm in PMMA for 2.0 MeV protons) where the maximum amount of energy is deposited. With high refractive index layer acting as the core surrounded by a lower refractive index cladding (the unmodified PMMA), light guidance is achieved. In the second case we spin coat dye doped PMMA on a suitable substrate (lower index than PMMA) and irradiated with focused proton beam. On developing with suitable chemical solution the irradiated parts are removed leaving alone the non-irradiated parts. Waveguides are formed by subsequent coating of a lower index material (preferably UV curable) followed by cutting and polishing. The waveguides can also be fabricated with imprinting technique with a suitable master stamp. The latter procedure can result in mass replication of waveguides and other structures in nonlinear polymers.

Polymer based solid state lasers which are cost-effective and free of maintenance find numerous applications in communication and sensing systems. The integration of optical transducers is one of the key issues in the development of 'lab-on-a-chip' micro-systems. For such applications polymer based components are an attractive alternative to more commonly used types of solid state lasers. Most of the earlier work on solid polymer and other solid state matrices containing laser dyes rely on external and macroscopic laser cavities. However, recently a group at Technical University of Denmark has developed solid state micro-laser cavities with triangular and trapezoidal shapes. The dimensions of the cavities were in the range of few hundred microns and such lasers find useful unique applications. They used the techniques of deep reactive ion etching and thermal imprint lithography.

There have been some interesting earlier reports of imprinting in rhodamine doped PMMA. Nilsson et al. successfully doped PMMA with R6GClO₄ and utilizing the thermal imprinting technique fabricated solid state micro-cavity dye laser [45]. Rhodamine B is not stable and will degrade with higher temperature while R6GClO₄ is a more robust dye. The stamp used for imprinting has been fabricated using optical lithography and reactive ion etching processes. Tunable microfluidic dye lasers have also been fabricated in SU8 using similar procedures [46-50]. Compared to their technique we expect direct writing with a proton beam will yield smoother and better side walls.

Several Possibilities with PBW include:

- (a) Direct writing of Waveguides, Ybranches, Gratings, and other structures in dye-doped (Rhodamine, Disperse Red, and Porphyrins) thick PMMA and/or SU-8 (up to 10 μm). Disperse Red doped polymers combined with electrical or optical poling are potential candidates for high-speed electro-optic modulators. Porphyrin doped polymers are useful in ultrafast optical switching and limiting applications.
- (b) Imprinting of the above mentioned structures in thin PMMA films (few 100 nm) on suitable substrates from a metallic stamp (e.g. nickel) fabricated using PBW
- (c) Fabrication of solid-state dye doped micro-lasers in RhB/R6G doped thick PMMA/SU-8 films using direct write or alternatively imprinting the laser structure (in case of PMMA only) and integrating the laser with waveguides or microfluidic channels for device applications.

Table 1 summarized the potential of the combined techniques of proton beam writing and imprinting for producing various possible structures in dye-doped PMMA and SU8.

1(c) NONLINEAR OPTICAL CRYSTALS

Nonlinear optical crystals such as KTiOPO₄ (KTP), LiNbO₃, BaB₂O₄ (BBO), and BiB₃O₆ (BIBO) are crucial in achieving compact tunable laser sources in the visible and near-infrared using frequency conversion techniques like second harmonic generation, difference frequency generation, and optical parametric oscillation [50]. It is well established that light confinement is much higher in waveguide geometry compared to bulk crystals thereby enhancing the efficiency of frequency conversion process. Also, performance in channel waveguides is better than planar type due to better confinement. Conventional techniques for fabricating waveguides in optical crystals include diffusion, ion exchange, pulsed laser deposition, and implantation [51]. Among these, implantation has been the most widely used method for achieving waveguides in nonlinear crystals [52,53]. However, most of these

techniques are optimized for producing planar waveguides. Moreover, most of the earlier studies focused mainly on fabricating waveguides and very few on the actual frequency conversion experiments.

Potassium Titanyl Phosphate [K₂TiOPO₄] or KTP is an excellent nonlinear crystal with high nonlinear coefficient ($d_{33} = 16.9$ pm/V at 1.064 μm), broad transparency, high temperature tolerance, large angular bandwidth, and relatively high laser damage threshold. It has been widely applied to generate green light (532 nm) by frequency-doubling either Nd:YAG or Nd:YVO₄ in the near-infrared. For type II Second Harmonic Generation of 1.064 μm radiation, KTP has broad angular acceptance and large temperature bandwidth making it well suited either inside or outside of the laser cavity. Phase matching for this 0.532 μm output at $\phi = 23.3^\circ$ and the walk-off angle is 0.2° . Conversion efficiencies can exceed 65 percent in the bulk crystal. KTP is also effective for optical parametric oscillator applications. KTP has low dielectric constants compared to materials with comparably high electro-optic coefficients. This combination of properties makes KTP potentially attractive for optical waveguide devices, including phase modulators, amplitude modulators and directional couplers. BiBO has some of exceptional properties like large effective nonlinear coefficient ($d_{22} = 2.2$ pm/V), broad phase matching range (410 nm to 2100 nm) with useful optical transmission from 200 nm to 2100 nm. BBO is of particular importance in the visible for generation of UV light. BiBO is a relatively new nonlinear optical material with a large effective nonlinear coefficient (compared to BBO and KTP) for Type I second harmonic generation. With its high laser damage threshold and inertness to moisture, BiBO possesses the right mixture of attributes as an excellent crystal for frequency conversion to generate blue and green laser light. The optical transmission of BiBO extends from 2500 nm in the infrared down to ~ 280 nm in the UV. One of the major advantages of BiBO is that this biaxial crystal offers versatile phase-matching characteristics. The effective nonlinear coefficient of BiBO is ~ 3.2 pm/V at 1079 nm, which is larger than those of BBO and LBO, and comparable to that in KTP.

2. EXPERIMENT

Laser grade Rhodamine B, Rhodamine 6GClO₄ are purchased from Sigma Aldrich and used as is. Chloroform and other solvents are also purchased from Sigma Aldrich and are $>99\%$ pure. PMMA with molecular weight of 950,000 dissolved in Anisole (11% by weight) purchased from MicroChem [54] is used for spin coating thin layers (up to 10 μm) on GE124 (Fused silica, RI of 1.457) substrates. Su8-2005 was also purchased from MicroChem and used as is. The substrates are initially cleaned thoroughly using piranha etch and later dried and pre-baked on a hotplate to a temperature of 150° for about 30 minutes to remove the excess moisture present in the samples. These two measures ensure the enhancement of resist adhesion to the substrate. The preparation of solutions and spin coating are carried out in a Class 1000 clean room in order to reduce the chances of depositing unwanted particles on the samples. 1%, 2%, and 3% Rhodamine B is in 950 PMMA A11 (doped by weight percent) is spin coated on clean glass substrates for PBW. For SU8 waveguides SU8-2005 was spin coated on glass substrate (Marie nfeld, RI of 1.5177) at a speed of 1000 rpm for 30 seconds and post-baking was carried out at 90°C for about 3 minutes. Since SU8 undergoes cross-linking on exposure to light sufficient care was taken not to expose the samples after coating by placing them in a black box prior to writing the structures. For micro-lasers the SU8-2005 doped with RhB was coated on to a silicon substrate with chromium gold coating (used for better adhesion).

The experimental setup used to characterize the emission from micro-lasers is described as follows. We use a continuous wave laser at 532 nm (Diode Pumped Solid State) with a maximum output power of ~ 35 mW. The beam was not focused and incident directly on the micro-laser. The emission from the sample is collected using a fiber attached with a collecting lens. The output of the fiber was connected to a small USB spectrometer (Ocean Optics, Model USB2000) interfaced to a personal computer.

3. RESULTS & DISCUSSION

Figure 1(a) shows the schematic of the procedure for fabricating waveguides in polymers. PMMA being positive resist on exposure to proton beam the irradiated part is left over on the substrate while the un-irradiated parts are removed after developing. The doped PMMA solution is spin coated on to a suitable substrate (glass plate with

RI of 1.5177 or GE124 glass with RI of 1.457) resulting in films with thickness ranging from 4-8 μm . The sample is pre-baked and post-baked to remove any excess solvent present. PBW was carried out using the high-brightness 3.0 MeV Singletron facility at the Centre for Ion Beam Applications, National University of Singapore. A 2.0 MeV proton beam with focal spot size of $\leq 1 \mu\text{m}$ and ion doses of $\sim 10^{14}$ - 10^{15} ions/ cm^2 corresponding to a fluence of $\sim 90 \text{ nC}/\text{mm}^2$ was used to fabricate the waveguides. After irradiation the sample is developed in a solution of Isopropyl alcohol + de-ionized water (7:3 ratio) for about a minute. Figure 2(a) shows the schematic of the proposed nonlinear waveguide with doped PMMA forming the core with RI of ~ 1.50 and substrate RI being 1.457. A suitable polymer (UV curable) with RI of < 1.47 will be used as cladding followed by placing a glass cover for further protection. Finally the sample will be cut and polished for final use. Figure 2(b) depicts the computed fundamental mode profile of the proposed waveguide structure. The mode has been obtained using the BeampropTM software with the index values mentioned in figure 1(b). Figure 3 shows some pictures, obtained using an optical microscope, of the RhB doped PMMA ridges of 1 cm length. It is evident from the figure that direct writing of nonlinear polymers using the proton beam is feasible and this serves as a proof of our concept. We are in the process of choosing an appropriate cladding material (preferably UV curable). After coating the cladding material and curing we will cover the sample with a glass slide for protection and finally cleave and polish it.

Figure 4 illustrates the procedure for fabricating the waveguides in SU8 doped with nonlinear dye. Since SU8 is negative resist the irradiated part is removed after developing with suitable chemicals. Figure 5(a) shows the schematic of the proposed nonlinear waveguide with SU8 doped with RhB or R6G forming the core with RI of ~ 1.60 and substrate RI is 1.5177. NOA 88, a UV curable adhesive with RI of ~ 1.555 will be used as cladding followed by placing a glass cover for further protection. Finally the sample will be cleaved and polished for final use. Figure 5(b) depicts the computed fundamental mode profile of the proposed waveguide structure. The mode has been obtained again using the BeampropTM software with the refractive index values mentioned in figure 5(a).

Figure 6(a) shows the schematic of the micro-cavity and the corresponding angles involved. We used the same cavity design employed in ref. 50. At the output interface a reflection of 36.4 % is obtained. The output angle is 78.8° . The mirror applied to the silicon wafer consists of a chromium layer which is used to improve the adhesion of the gold layer. Figures 6(b) and (c) shows the optical microscope pictures of micro-laser cavities in SU8 doped with Rhodamine B. We fabricated two samples with several laser cavities on them each with dimensions of $200 \mu\text{m} \times 200 \mu\text{m}$ and $50 \mu\text{m} \times 50 \mu\text{m}$. A small skewing of the structure is visible at a couple of edges which could be a result of the beam scanning speed. Figure 6 (d) shows the emission spectrum of different samples. The yellow curve is the emission from thin film of PMMA doped with RhB while the violet curve is the emission spectrum from SU8 doped with RhB prior to proton beam irradiation. The blue curve is the emission obtained from proton irradiated micro-laser which is red shifted by few nm. It is clear from the figure that the tunability is large with these kinds of structures by employing different polymers. The proton beam fluence dependence on the shift of the emission wavelength is still under investigation. Figure 6(e) shows the emission spectra from SU8-RhB (1% doped by weight) micro-laser cavity. Due to non-availability of a pulsed laser source we used a cw source and we strongly feel that the peak powers are not sufficient for lasing within the cavity. However, at the peak of the emission spectrum we could see a possible laser action with the line width narrowing considerably. We are also planning for micro-lasers in PMMA doped with RhB and R6G. Combining both PMMA and SU8 with RhB/R6G we expect to achieve $\sim 100 \text{ nm}$ tunability in the 550-650 nm spectral range. For imprinting purpose we propose to use R6G instead of RhB for its robustness towards higher temperatures.

Fig. 7(a) shows the SRIM (Stopping Range of Ions in Materials) calculation of the range of 2 MeV protons inside BIBo crystal. As evident the end of range is at $\sim 38 \mu\text{m}$. The maximum damage occurs at this depth and hence the waveguide is formed at this depth. Figures 8(b) and 8(c) show similar calculations for KTP and Nd:YVO₄ giving waveguide depths of $\sim 34 \mu\text{m}$ and $42 \mu\text{m}$ respectively. Utilizing a high energy proton beam we shall write channel waveguides directly (without any mask) in nonlinear optical crystals of KTP, BIBO and laser crystal Nd:YVO₄. Our initial efforts in writing the waveguides were successful but the optical characterization part was unsuccessful because of the bad surface quality of the crystals we received and were not suitable for further characterization. We will investigate the linear optical properties of these waveguides at visible (633 nm) and telecom (1550 nm) wavelengths. The mode profiles, refractive index profiles, and propagation losses will be determined at both these wavelengths. The refractive index profile is extracted from the mode profile using near-field propagation method. The propagation losses will be determined using the standard scattering technique. The relationship between the proton dose, mode profile, and propagation loss will be investigated. Extensive results obtained from these experiments will be used for optimizing the writing of waveguides. The frequency conversion experiments will be carried out using

high power laser sources at corresponding phase matching wavelengths and their efficiencies will be evaluated and compared with previously obtained values in planar waveguides.

4. CONCLUSION

In conclusion we have demonstrated the proof of concept for direct writing structures into nonlinear dye doped polymers of PMMA and SU8. Proton beam writing combined with the technique of imprinting holds promise for future generation lithographies for mass production of micro- and nano-structures with highly cost-effective procedures. As discussed in the text there are several possibilities of fabricating different structures, both active and passive for use in optical communication and microfluidic applications. Waveguides in nonlinear optical crystals will extend the capabilities of compact and robust laser sources in the visible as well as near-infrared.

5. REFERENCES

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| Sample | Dye | Structure (size) | Doping | Technique |
|---------------------------------------|----------------------|------------------------------|---------------|------------------|
| PMMA (950K) in Anisole | Rhodamine B | Waveguide (μm) | 1 %, 2%, 3% | PBW |
| PMMA (950K) in Anisole | Rhodamine B | Waveguide (μm) | 1 %, 2%, 3% | Imprinting |
| PMMA (950K) in Anisole | Rh6GClO ₄ | Waveguide (μm) | 1 %, 2%, 3% | Imprinting |
| PMMA (120K) in Anisole | Rhodamine B | Grating (nm) | 1 %, 2%, 3% | PBW |
| PMMA (350K) in Anisole | Rhodamine B | Grating (nm) | 1 %, 2%, 3% | PBW |
| PMMA (120K) in Anisole | Rh6GClO ₄ | Grating (nm) | 1 %, 2%, 3% | Imprinting |
| PMMA (350K) in Anisole | Rh6GClO ₄ | Grating (nm) | 1 %, 2%, 3% | Imprinting |
| SU8-2005 in Cyclopentanone | Rhodamine B | Micro-laser(μm) | 1 %, 2%, 3% | PBW |
| SU8-2005 in Cyclopentanone | Rh6GClO ₄ | Micro-laser(μm) | 1 %, 2%, 3% | PBW |

Table 1 Matrix showing the potential of the combined techniques of proton beam writing and imprinting for producing various possible structures in dye-doped PMMA and SU8.

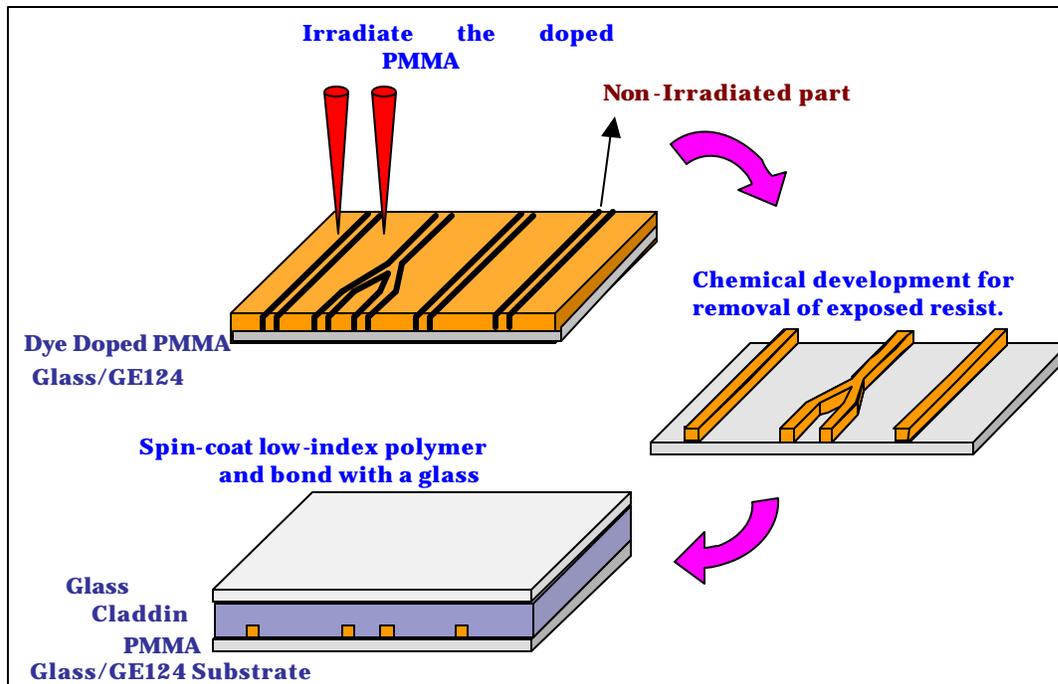
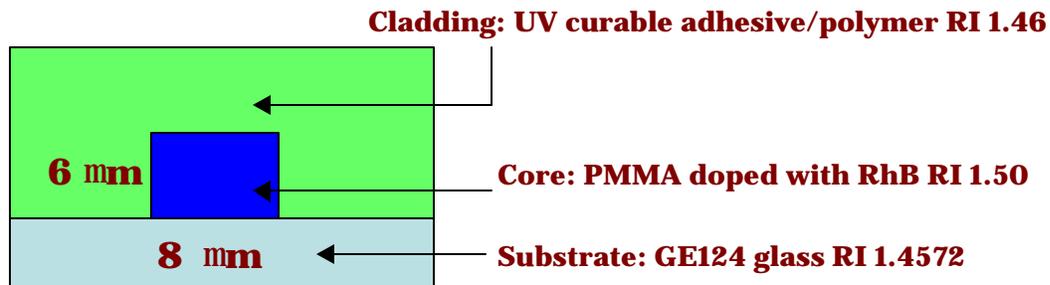
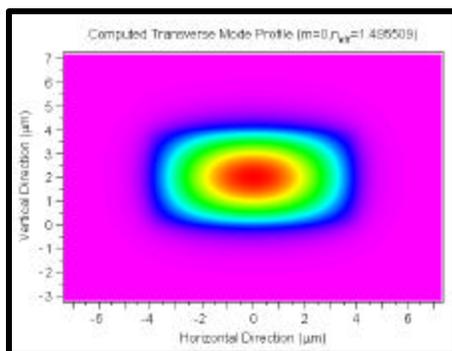


Figure 1 Fabrication of waveguides in PMMA doped with nonlinear dye such as Rhodamine B is shown schematically



(a)



(b)

Figure 2(a) Profile of the proposed nonlinear waveguide with $6 \mu\text{m} \times 8 \mu\text{m}$ dimensions. Refractive indices mentioned are at a wavelength of 633 nm **(b)** Computed first order mode profile using BeamProp™ with the refractive indices mentioned in (a)

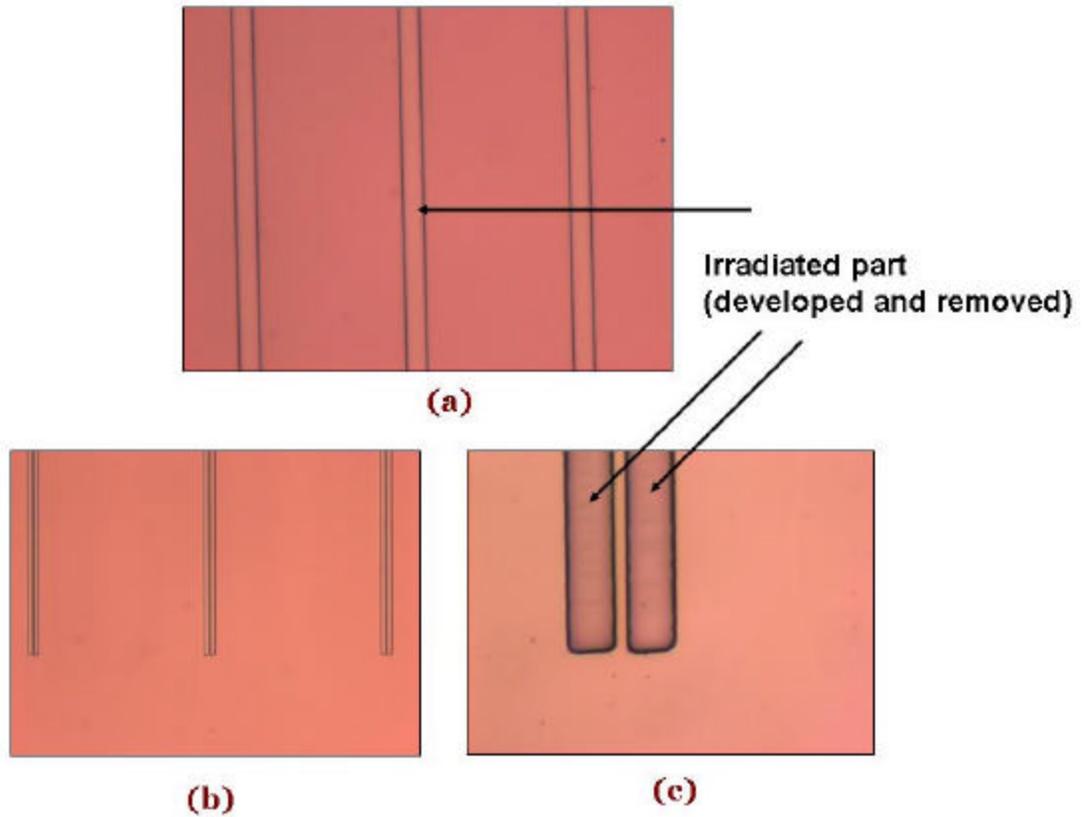


Figure 3(a) Pictures from optical microscope of the sample after proton beam irradiation and developing. **(b)** Three waveguide (core) structures in PMMA (950K) doped (1% by weight) with Rhodamine B. The irradiated parts are removed from the sample leaving out the un-irradiated parts. **(c)** Close up picture of the waveguide core (PMMA+RhB). We expect very smooth side walls using this technique implying lower scattering losses in the waveguide.

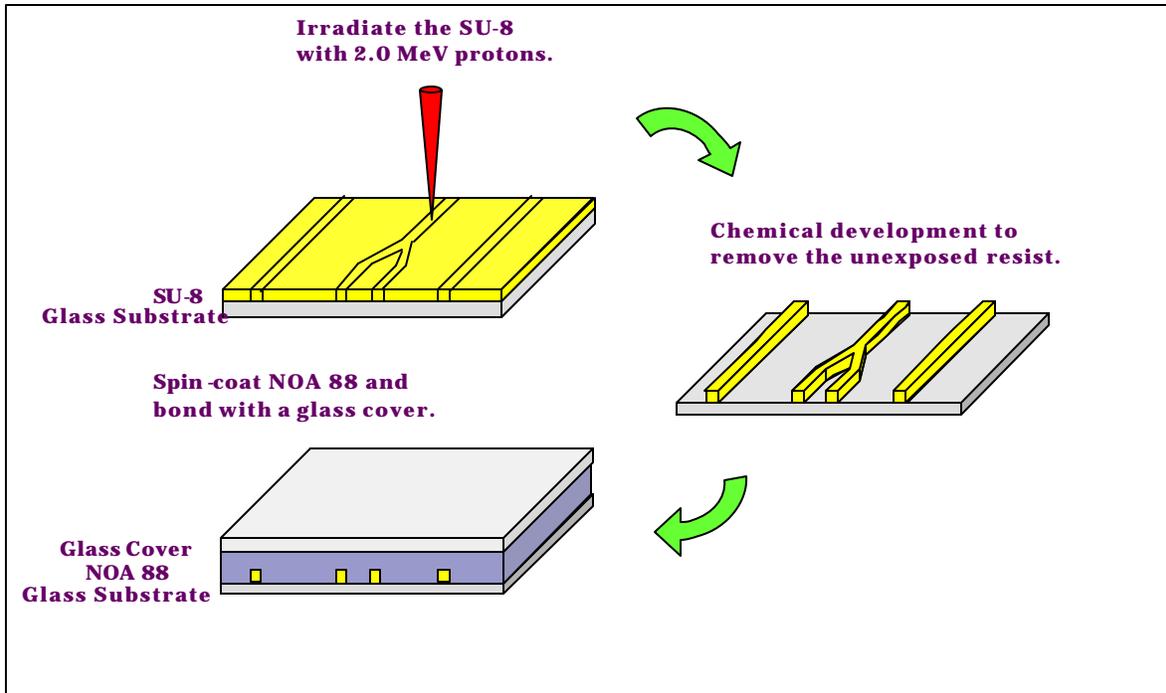
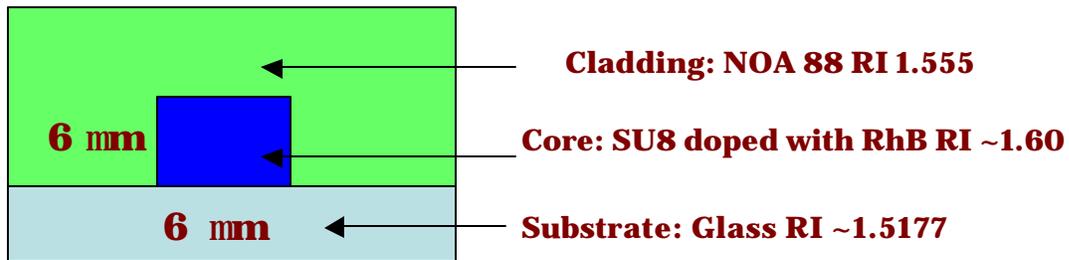
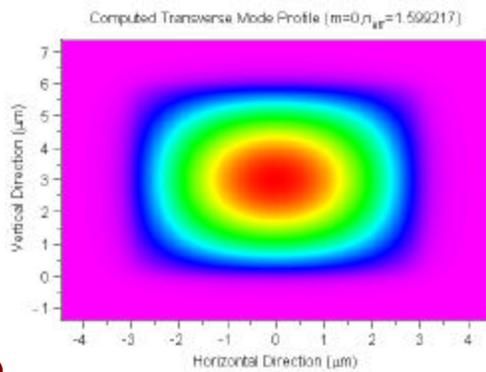


Figure 4 Fabrication of waveguides in SU8 doped with nonlinear dye (e.g. Rhodamine B) is shown schematically



(a)



(b)

Figure 5(a) Profile of the proposed nonlinear waveguide in SU8 with $6 \mu\text{m} \times 6 \mu\text{m}$ dimensions. Refractive indices mentioned are at a wavelength of 633 nm **(b)** Computed first order mode profile using BeamPropTM with the refractive indices mentioned in (a)

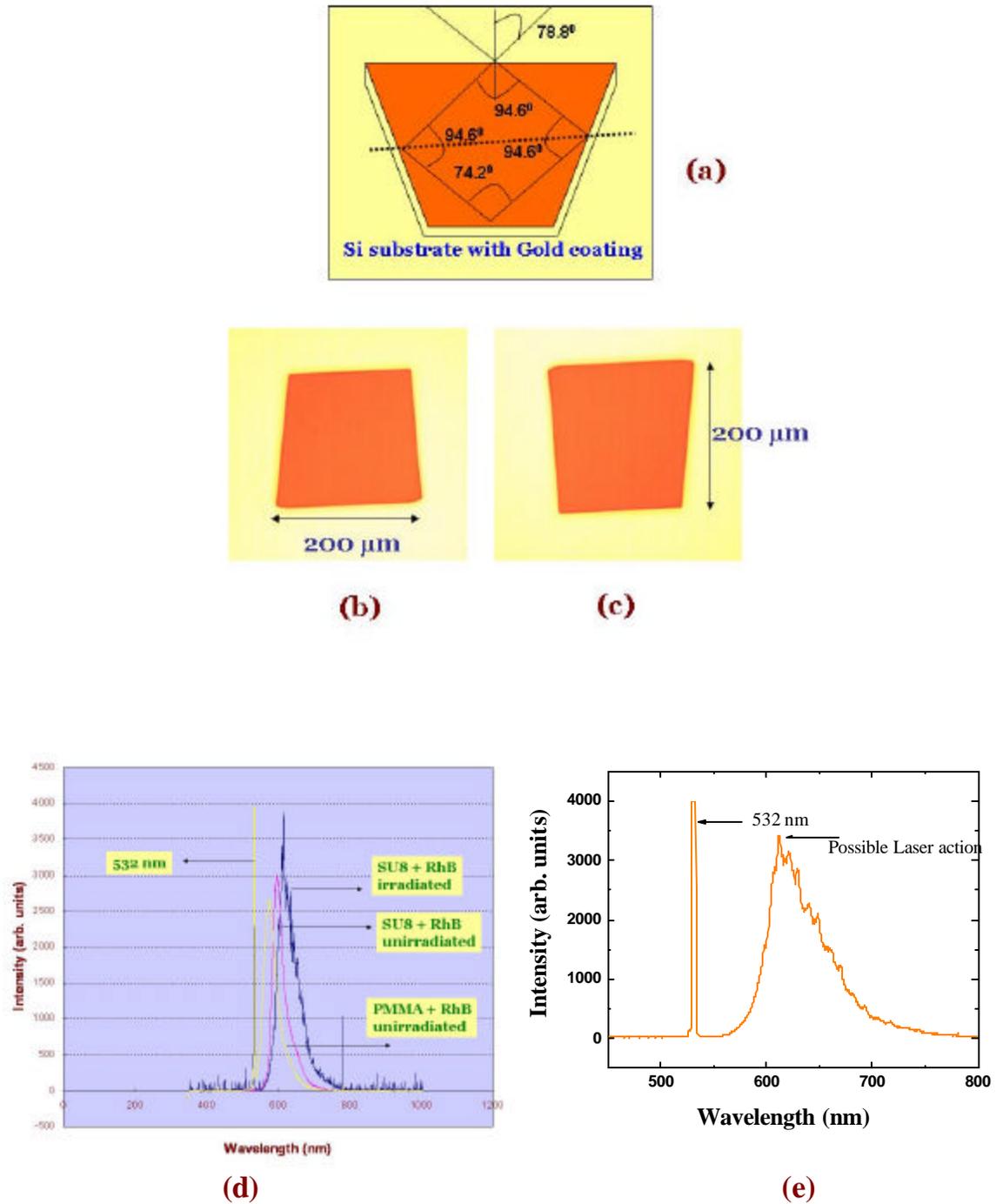


Figure 6(a) Schematic of the micro-laser cavity as described in the text and reference 50. **(b)** & **(c)** Pictures from optical microscope of micro-laser cavities in SU8-2005 doped with Rhodamine B (1% by weight) on a silicon substrate coated with layer

of gold (for better adhesion). **(d)** Emission spectrum from the micro-laser pumped with 532 nm continuous wave laser light. A sharp peak at the centre indicates possible laser action.

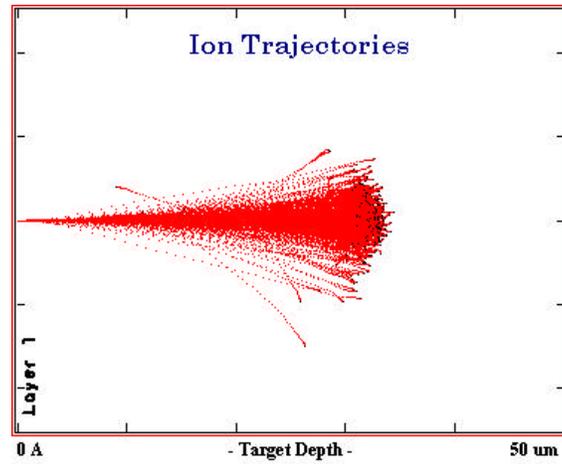


Figure 7(a) Trajectory of 2.0 MeV protons inside the BiB₃O₆ crystal as a function of depth. End of range ~34 μm

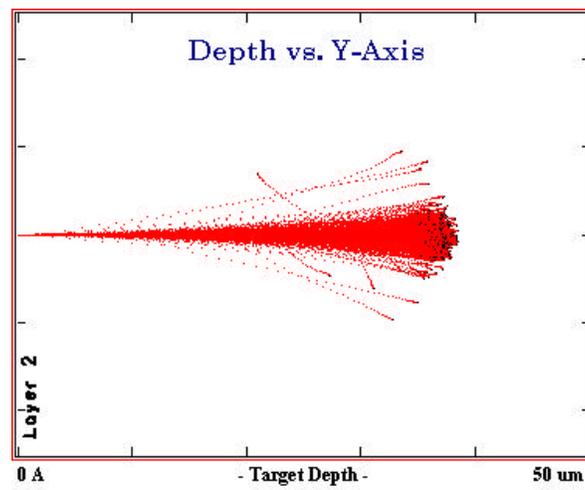


Figure 7(b) Trajectory of 2.0 MeV protons inside the KTP crystal as a function of depth. End of range ~38 μm

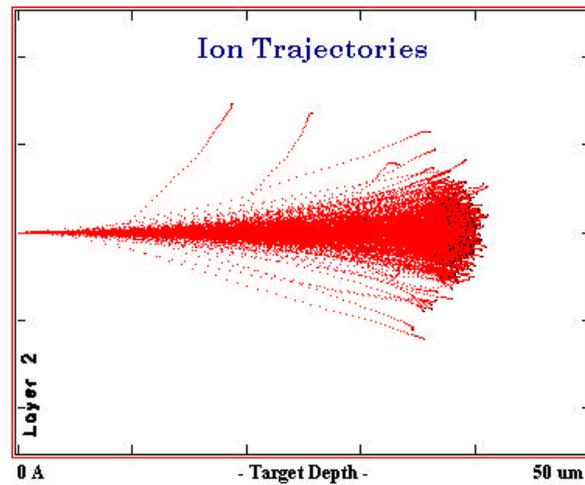


Figure 7(c) Trajectory of 2.0 MeV protons inside the Nd:YVO₄ crystal as a function of depth. End of range ~40 μm