Fabrication and characterization of diffraction gratings in ophthalmic polymers by using UV direct laser interference patterning

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Introduction

Vision correction has been ‘hot topic’ in research throughout the last centuries

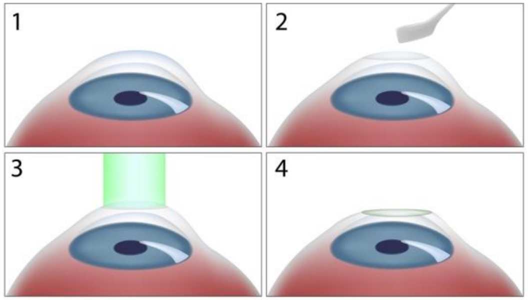
Development of excimer lasers → Photo-refractive surgery

Main techniques:

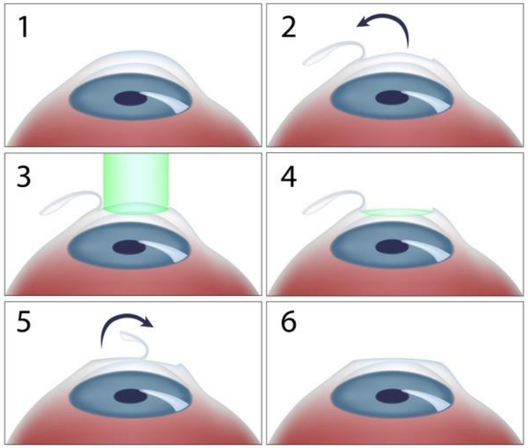
- Photo-Refractive Keratectomy, PRK
- LAser in SItu Keratomileusis, LASIK
- Small Incision Lenticule Extraction (ReLEx SMILE)

Aim:

- ➢ Reshape the cornea through photo-ablative decomposition processes
- ➢ Destructive, invasive and irreversible techniques
- ➢ Postsurgical complications and secondary visual effects



Photorefractive Keratectomy (PRK)



Lasik Eye Surgery

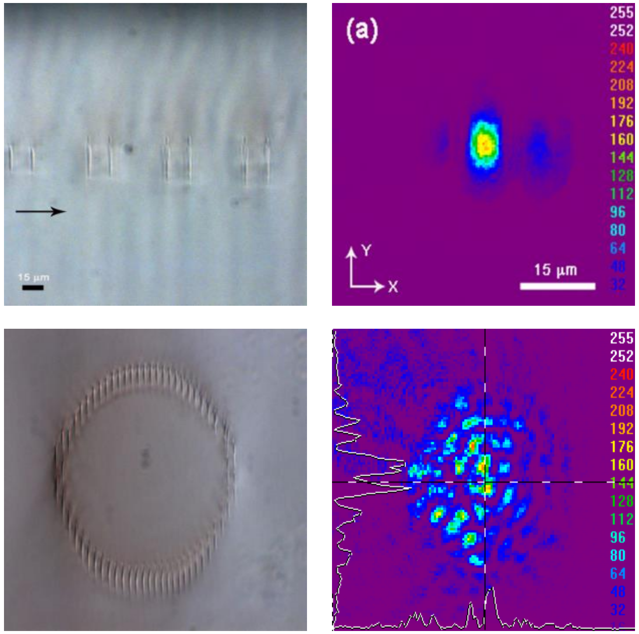
http://www.lasereyesurgeryhub.co.uk/lasik-vs-lasek-vs-prk/

Introduction

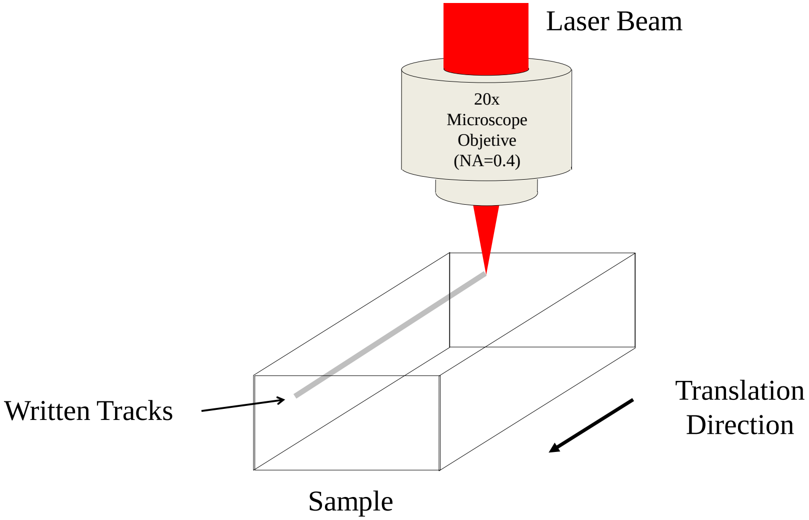
A new approach to refractive correction based on Ultrafast Laser Inscription, ULI

Ultra-short laser pulses are focused inside the material → Refractive index modification

Passive and active photonic devices: Waveguides, beam splitters, diffraction gratings, etc.



$\Delta n \sim 1\times10^{-4}$ to 1×10^{-2}



- D. Sola et al., “Stress-induced buried waveguides in the $0.8CaSiO_3$-$0.2Ca_3(PO_4)_2$ eutectic glass doped with Nd^{3+} ions”, Appl. Sur. Sci. 278 (2013) 289-294.
- J. Martinez de Mendibil, D. Sola et al. “Ultrafast direct laser writing of cladding waveguides in the $0.8CaSiO_3$-$0.2Ca_3(PO_4)_2$ eutectic glass doped with Nd^{3+} ions”, J. Appl. Phys. 117 (2015) 4906963.
- D. Sola et al., “High-repetition-rate femtosecond laser processing of acrylic intra-ocular lenses”, Polymers 12 (2020) 242.

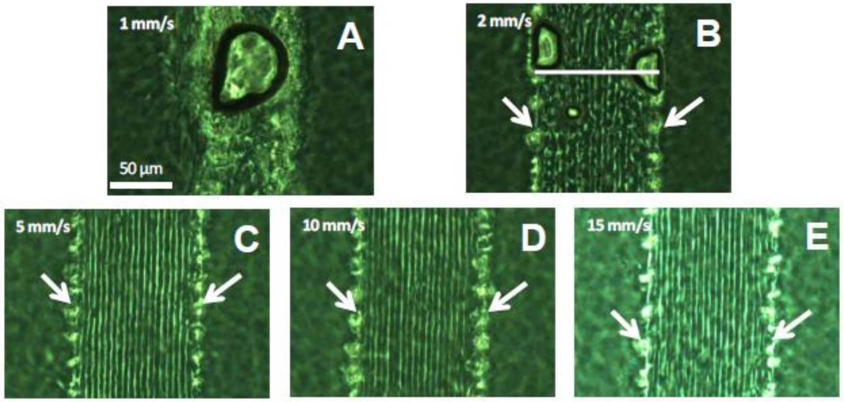
Introduction

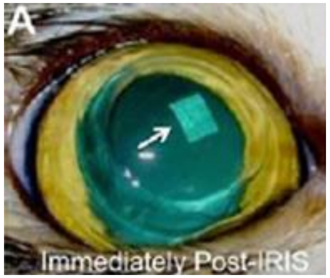
Knox et al. (Rochester University) developed Intra-tissue Refractive Index Shaping technique, IRIS (2006 to date)

Refractive index modification was induced by high-repetition-rate laser pulses below damage threshold

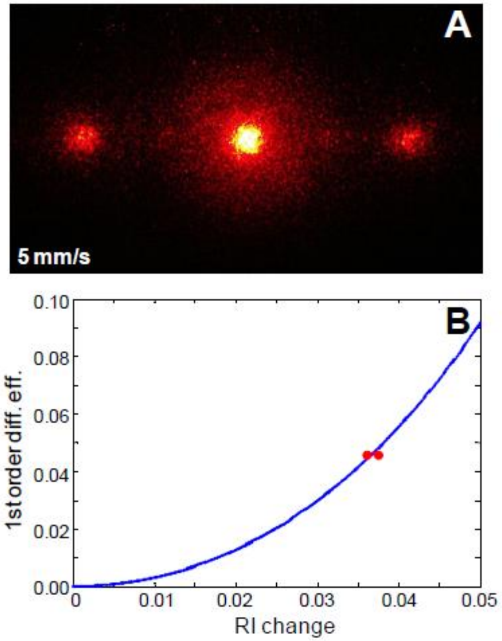
- Dye-doped and non-doped silicone-based and non-silicone-based hydrogel polymers
- *Ex vivo* dye-doped and non-doped corneas
- *In vivo* corneas (live cats)

$\Delta n \sim 2.1\times10^{-2}$ to 3.7×10^{-2}
max. scanning speed: 20 mm/s (8 μm/s in live cats)





Cylinder: -1.4±0.3 D
Defocus: -2.0±0.5 D
HORMS: 0.31±0.04 μm



Introduction

There are 2 main drawbacks:

- Knowledge about the nature of the refractive index change in the corneal stroma
- The small scanning speed achieved so far ➡ unviable at real scale

Example:

IRIS:
Beam diameter: 1-3 µm
Scanning speed: 20 mm/s

Processing time

Let´s suppose a 5x5 mm^2 linear diffraction grating with 5 µm inter-line spacing (similar dimensions to that of the cornea)
IRIS: $\mathbf{t_{15} = 250\ s}$

Introduction

Aim

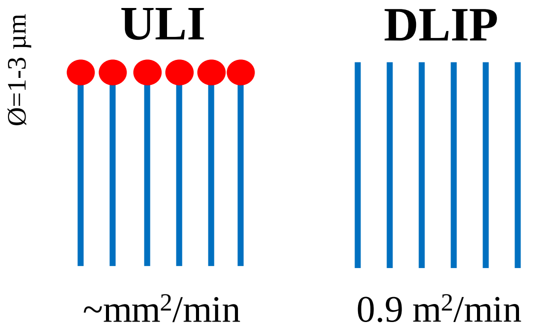
To use interference techniques to create diffractive devices

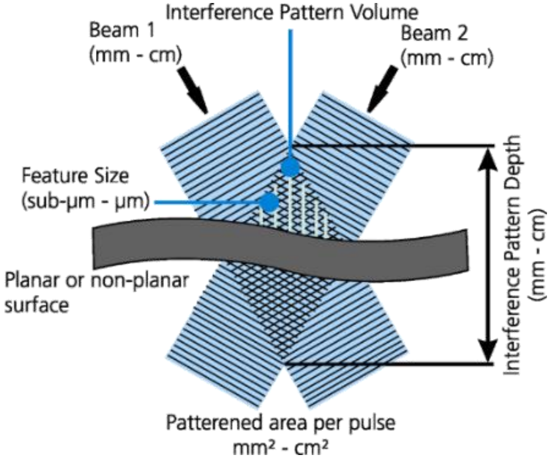
Direct Laser Interference Patterning technique, DLIP

- Non-contact
- Single step
- Processing speeds up to 0.36 m²/min (metals) and 0.9 m²/min (polymers)
- Easy to implement in manufacturing processes

Geometry controlled by α, λ, I

$$d = \frac{\lambda}{2 \cdot \sin\alpha} \qquad I_P(x,y) = 4I_L\cos^2\left(\frac{2\pi}{\lambda}x\sin\alpha\right)$$

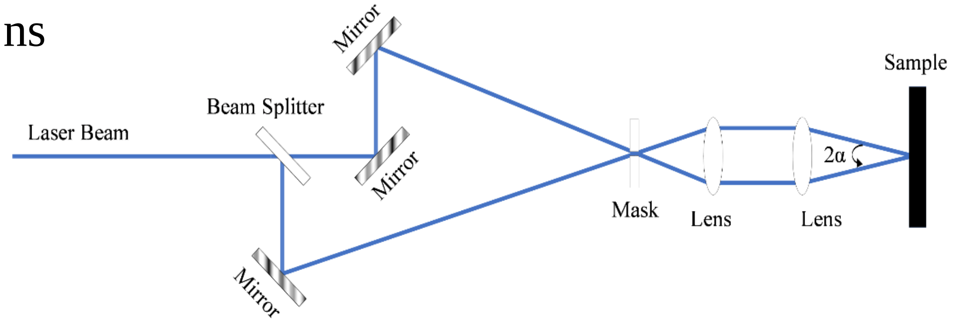




Experimental

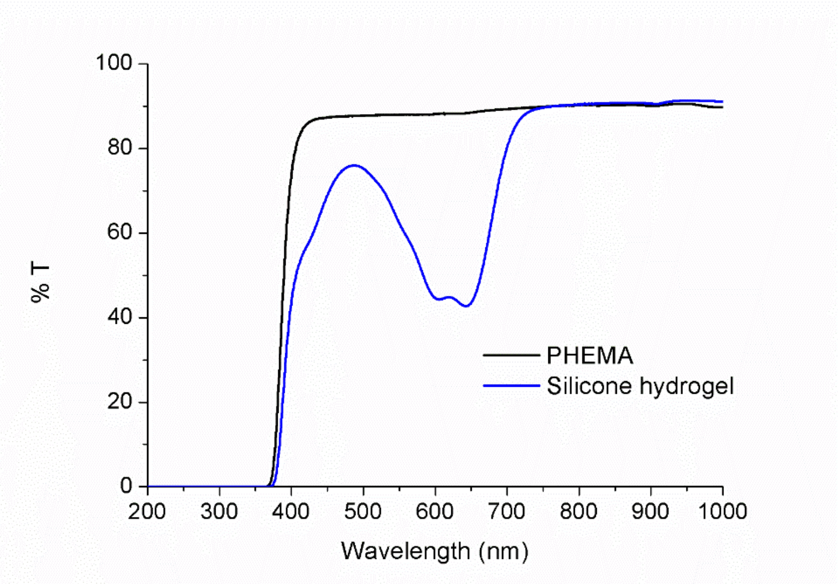
Laser source

- ➢ Q-switched Nd:YAG, 266 nm, 10 Hz, 10 ns
- ➢ Λ: 2.6 μm and 4.7 μm
- ➢ Fluence: 0.5 J/cm^2 – 17 J/cm^2
- ➢ No Pulses: 1 – 5



Materials

- ➢ Poly-hydroxyethyl-methacrylate, PHEMA
- ➢ Safrofilcon A (silicone hydrogel)



Characterization techniques

- ➢ Confocal microscopy
- ➢ Phase contrast and bright field microscopy
- ➢ FEG-SEM with EDX detector
- ➢ Micro-Raman spectroscopy
- ➢ Diffractive techniques

Results and discussion

Laser structuring

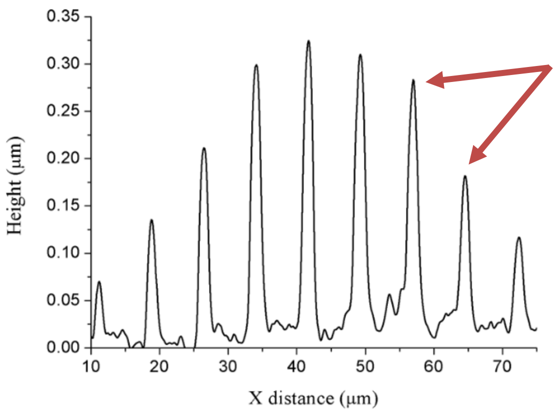
- Periodic line-like patterns were structured

High optical absorption @266 nm and long pulse duration (ns)

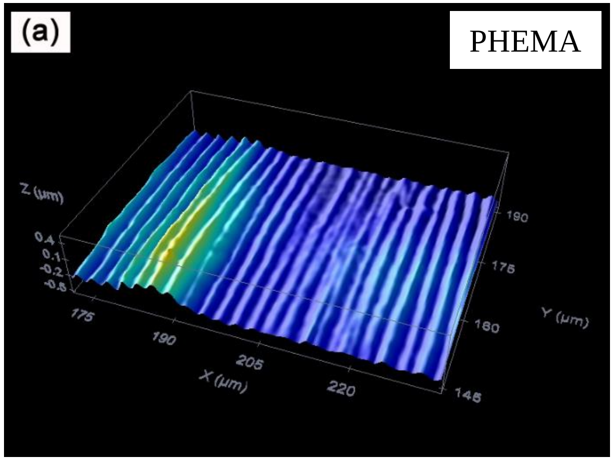
Photo-chemical Photo-thermal

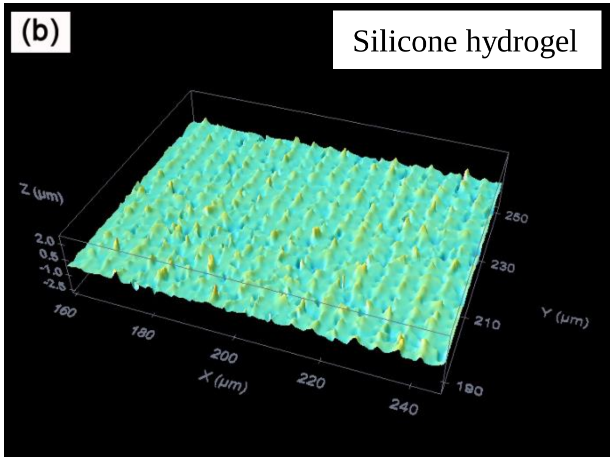
- At low laser fluence

Swelling of the polymer surface



Surface softening
&
Material expansion



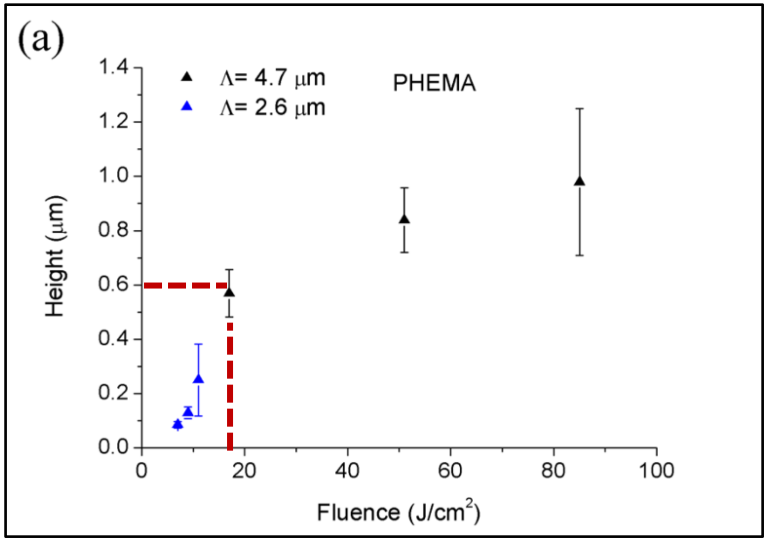


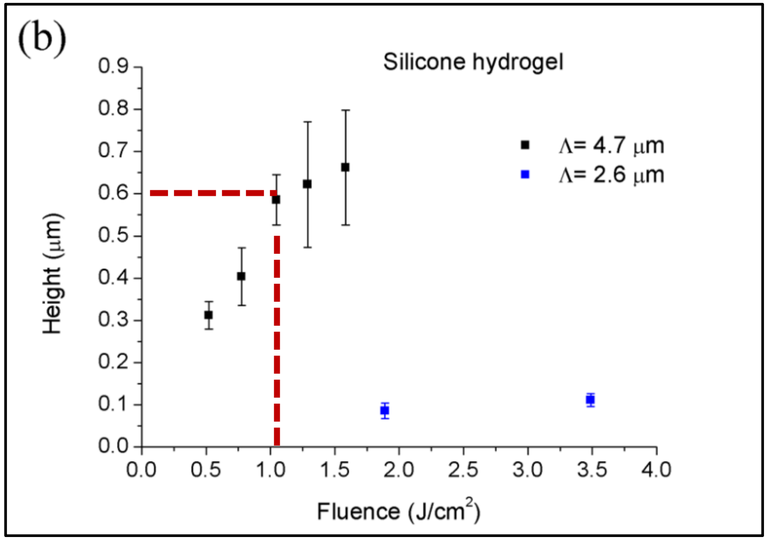
Results and discussion

Laser structuring

- Height of DLIP structures
  - ➢ Increased with laser fluence
  - ➢ The shorter the Λ, the lower the height

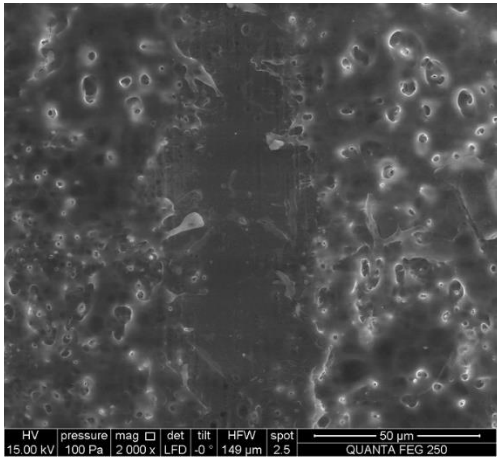
Optimal fluence to structure the silicone hydrogel polymer much lower than PHEMA





- High laser fluence

Formation of a Heat Affected Zone, HAZ

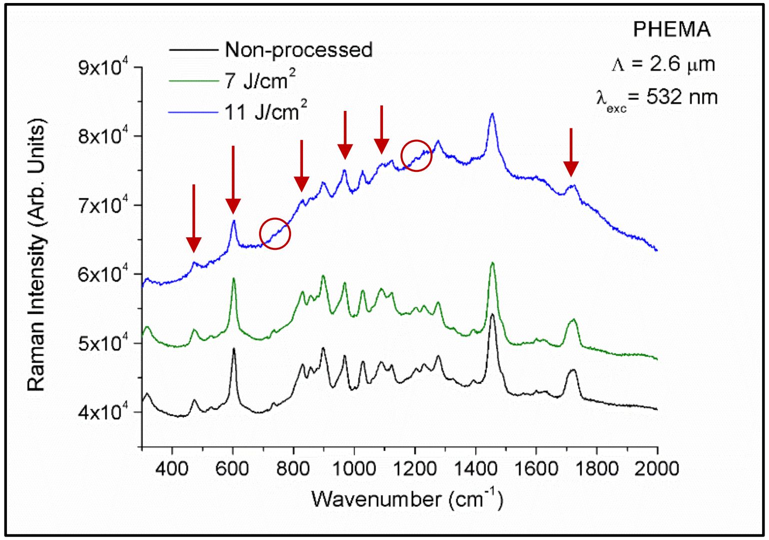


Results and discussion

Micro-Raman characterization

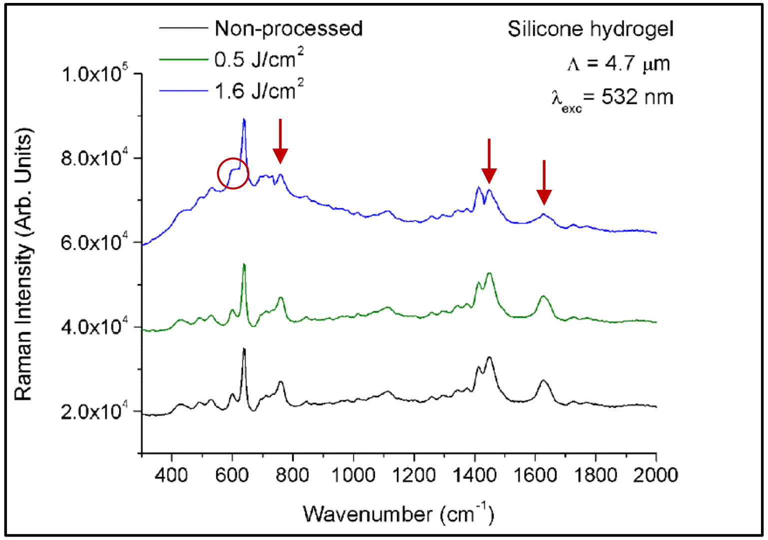
- At high fluence
  - ➢ Severe decrease of peak intensity
  - ➢ Strong fluorescence background increase

➡ **Thermal decomposition**



- At low fluence
  - ➢ Polymer structure remained almost unaltered

➡ **Additional cross-linking**



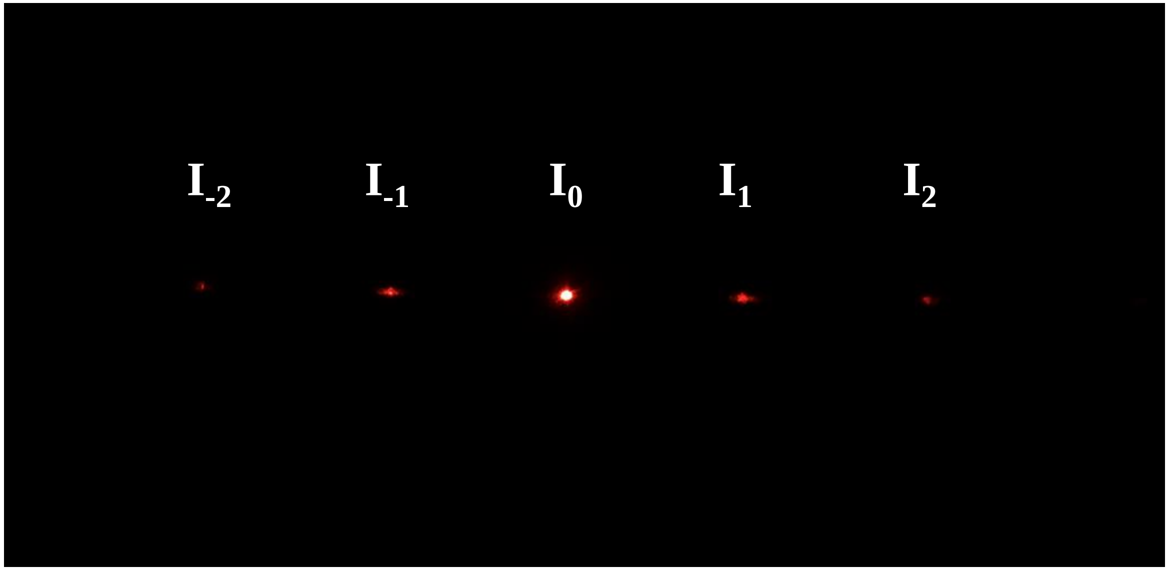
Results and discussion

Optical characterization

- Illumination under cw He-Ne laser @632.8 nm

- Diffraction angles showed good agreement with the diffraction equation:

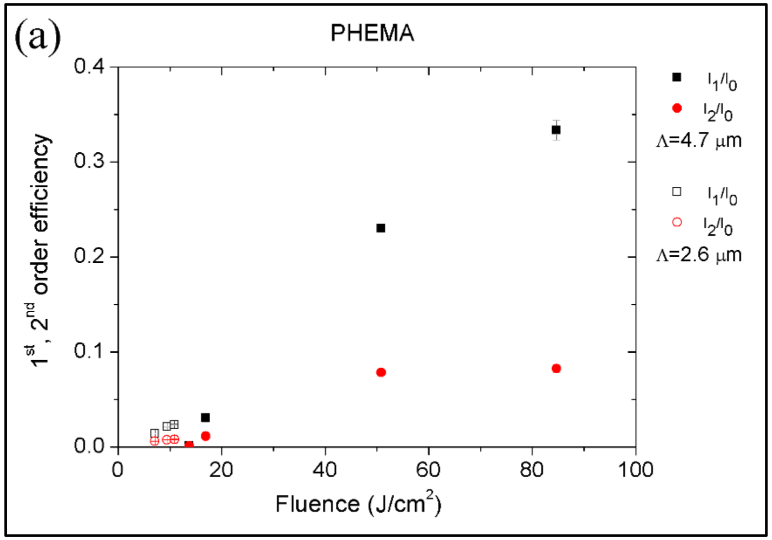
$$m \cdot \lambda = d \cdot \sin \theta$$



Results and discussion

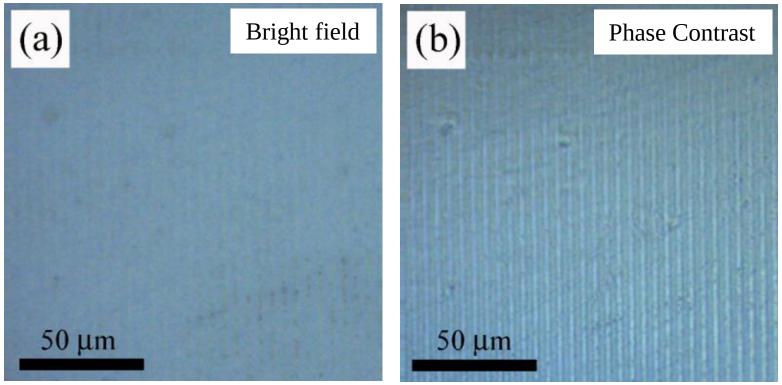
Optical characterization

- 1st and 2nd-order efficiency
  - ➢ Increased with fluence
  - ➢ Followed a linear trend
- Total efficiency
  - ➢ Highest values achieved at low fluence and Λ= 4.7 µm
  - ➢ Low scattering losses ≥ 98%



Silicone hydrogel

Λ (µm)	F (J/cm^2)	Efficiency
4.7	0.5	0.989 ± 0.007
4.7	0.8	0.981 ± 0.008
4.7	1.0	0.896 ± 0.010
4.7	1.3	0.742 ± 0.033
4.7	1.6	0.632 ± 0.027
2.6	1.9	0.958 ± 0.026
2.6	3.5	0.332 ± 0.032



Results and discussion

Optical characterization

- Considering the diffraction grating as a phase grating and assuming a uniform "top-hat" shape index change within the irradiated region, then:

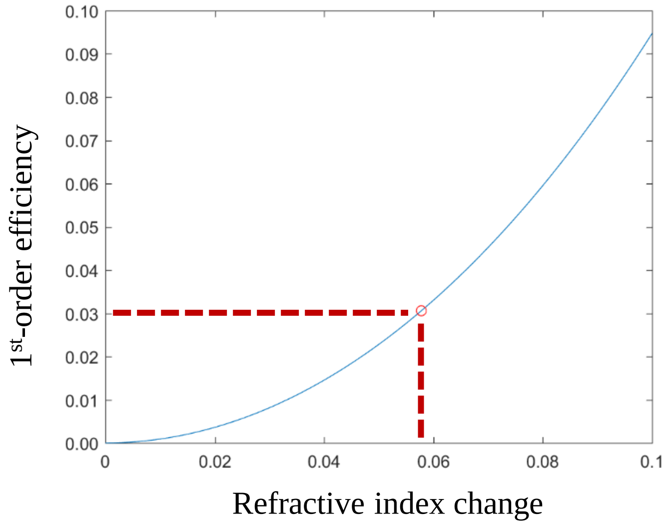
$$I_0 = \left(\frac{1}{\lambda z}\right)^2 \left[\left(e^{i2\pi\frac{(n+\Delta n)b}{\lambda}} - e^{i2\pi\frac{nb}{\lambda}}\right)\frac{a}{d} + e^{i2\pi\frac{nb}{\lambda}}\right]^2$$

$$I_1 = \left(\frac{1}{\lambda z}\right)^2 \left[\left(e^{i2\pi\frac{(n+\Delta n)b}{\lambda}} - e^{i2\pi\frac{nb}{\lambda}}\right)\frac{a}{d}\sin c\left(\frac{a}{d}\right)\right]^2$$

- 1st to 0th diffraction efficiency, I_1/I_0
  - ➢ PHEMA
    0.0013 (14.0 J/cm^2) and 0.307 (17 J/cm^2)
  - ➢ Silicone hydrogel
    0.0062 (0.5 J/cm^2) and 0.0272 (0.8 J/cm^2)

Refractive index change, Δn :

- ➢ PHEMA
  7.8×10^{-2} (14.0 J/cm^2) and 5.6×10^{-2} (17 J/cm^2)
- ➢ Silicone hydrogel
  5.3×10^{-2} (0.5 J/cm^2) and 8.5×10^{-2} (0.8 J/cm^2)



Conclusions

- DLIP under 2-beam configuration, with laser pulses at 266 nm and 10 ns pulsewidth, was successfully applied to structure PHEMA and silicone hydrogel polymers used as soft contact lenses.
- At low laser fluences it was observed that laser-matter interaction process in both polymers resulted in the swelling of the polymer surface.
- Height of DLIP structures increased with laser fluence and spatial period. However, high laser fluences induced a HAZ.
- Micro-Raman analyses showed that at low laser fluence material structure remained unaltered but at high fluence material underwent thermal degradation.
- DLIP structured areas showed diffraction patterns at both spatial periods.
- First- and second-order efficiency increases linearly with laser fluence. Nevertheless, only samples processed at the lowest laser fluences achieved total efficiency equal or higher than 98%.
- Refractive index modification for low scattering diffraction gratings was found to be between 5.3×10^{-2} and 8.5×10^{-2}.
- These values were similar to those reported by using the ULI technique but with an improvement of the processing yield of more than two orders of magnitude.

MARIE CURIE ACTIONS

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DFG Deutsche Forschungsgemeinschaft
German Research Foundation

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Thank You