mr-I T85 Series: Cyclic Olefin Copolymer (COC) Formulation for the Fabrication of Sub-Micron Thin Films

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ABSTRACT

Cyclic Olefin Copolymers (COCs) are well-known polymers suitable for a broad variety of different applications in diverse industrial sectors. Such scopes of applications reach from quite trivial usage like food packaging to rather high-tech applications like optical thin films for sensor systems or the manufacturing of micro-electro-mechanical systems (MEMS) and micro total analysis systems (µTAS). The deposition of COC thin films with several microns or sub-micron thickness via spin-coating is often required for the manufacturing purposes of such technological devices. In the following we will give a short overview on different applications for thin film COC usage and we will comment on some general beneficial material characteristics of this outstanding polymer class.

INTRODUCTION

There is growing industrial interest in replacing glass for various optical and medical applications. Main driving forces are the reduction of manufacturing time, to simplify the overall complexity of the production process, as well as a weight and cost reduction of the final device especially when single-use and disposable devices are envisaged. One interesting option to address these challenges for many applications is the integration of so called optical polymers (OPs). Such OPs are typically common thermoplastic polymers like polymethyl methacrylate (PMMA), polystyrene (PS), or polycarbonate (PC) with defined physico-chemical parameters like a defined glass transition temperature or intrinsic solubility characteristics. Most recent applications of such OPs derive for instance from the field of life-science for microfluidic applications and micro-optical components. Especially in the field of micro-fluidics alkaline and acidic stable devices and materials are often an essential requirement, where such generic OPs often suffer from limitations. Furthermore, many lithographic fabrication methods of micro-optical and microfluidic components require OPs which are chemically stable in subsequently performed processes like additionally deposited formulations for multi-layer approaches, and different chemicals, solvents, or developers, respectively. Cyclic Olefin Copolymers (COCs) address many of the mentioned requirements. Due to their chemical structure and nature COCs provide an outstanding chemical stability beside stable optical characteristics, making them suitable for many of the aforementioned applications. But the commercial availability of COCs is physically limited as powder, pellet, thermoplastic foil, or sheet based foils commercially distributed and manufactured under the registered trade names of e.g. Topas® or Zeonex®. For the manufacturing of extremely thin COC polymer films of a few microns or even beyond one micron film thickness, usually low concentrated polymer solutions in appropriate organic solvents are required which can be deposited via different thin film manufacturing techniques like spin-coating, doctor blading, or gravure coating. If specific micro- or nanostructures will be fabricated by the use of such COC thin films, a contamination of particles needs to be avoided and appropriate fine filtration steps have to be conducted. Hence, the manufacturing industry is heavily searching for such COC formulations which are ready-to-use solutions for e.g. spin-coating applicable without further preparation or cleaning steps.

SOLUTION

The material class of COCs has gained a lot of attraction for several industrial applications due to the outstanding chemical, optical, as well as mechanical characteristics of these amorphous thermoplastic polymers. COCs consist of norbornene and ethylene repetition units (see Fig. 1), are completely aliphatic and, hence, provide some intrinsic material properties which are typically not provided by more generic polymer classes like PMMA, PS, or PC.

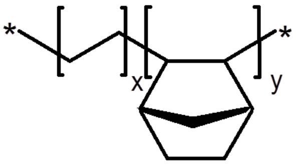

Fig. 1.
General chemical structure of cyclic olefin copolymers COCs.

COCs offer a high glass-like transparency beside exceptional low autofluorescence, an excellent water barrier characteristic with low moisture absorption, high mechanical rigidity and strength, outstanding chemical stability under alkaline and acidic conditions, superior biocompatibility, and overall good electrical insulation properties. Even more, the solubility characteristic of COC is different to more generic polymers like PC or PMMA, where polar organic solvents are applied. In contrast, COC shows best solubility characteristics in only a small number of non-polar organic solvents in which other OPs are insoluble. Therefore, COCs can be principally applied in multilayer polymer stacks or other processes where more than one subsequently deposited thin film is required. This combination of unique material properties of COCs highlight them as perfect polymers for a large number of different applications in e.g. medical devices, packaging industry, as well as active and functional materials for optics and electronics devices. Many of these new applications require for submicron thin films of such COC polymers. Due to the specific chemical structure and the resulting solubility characteristics of COCs the fabrication of formulations for submicron film thickness is often not trivial. One technological way for producing thin films of thermoplastic materials is spin-coating of a defined concentration of a polymer in an appropriate solvent. The concentration of the polymer in the particular solvent defines the final film thickness on the target substrate after spin-coating. Usually, solvents like toluene or other aromatic solvents are applied for COC, which are considered to be toxicological relevant and, hence, not easily capable of being integrated into industrial high volume manufacturing processes. Therefore, micro resist technology GmbH provides a thin film formulation where a less toxic solvent is used to adjust the desired COC film thickness via spin-coating. micro resist technology GmbH has built up a great knowledge database during the past years in the fabrication of such thin film COC formulations as well as the key production step of fine filtration which is required for particle sensitive processes and applications. Especially if the thermoplastic polymer is applied in the so called Nanoimprint Lithography (NIL, see Fig. 2), a particle free thin film after spin-coating is required. But thin film formulations of such COCs are not only limited to that nano-structuring technology.

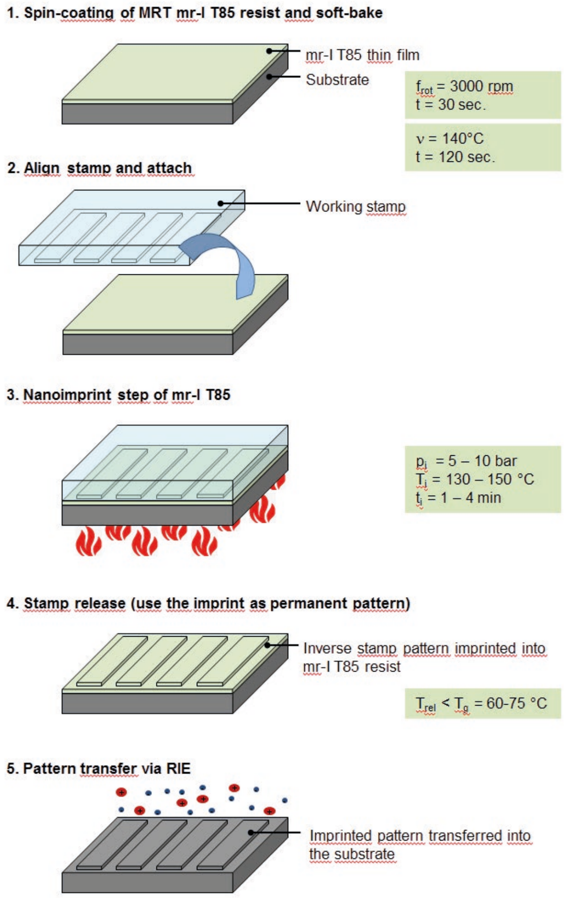

Fig. 2. Process scheme of thermal nanoimprint lithography with mr-I T85.

In fact, we notice great interest for certain applications where no nano-patterning is required at all but the intrinsic physico-chemical material characteristics of the COC polymer thin films are relevant as important building blocks for the final devices. Such special material requirements mainly derive from microfluidic and bio-applications as well as optical devices. micro resist technology GmbH is manufacturing and providing polymer formulations for the realization of thin films via spin-coating with 300 nm, 1 µm, and 5 µm thickness. The formulation series has the trade name mr-I T85 and is made of a special kind of COC with a glass transition temperature (Tg) of 78 °C and optimized flow-ability characteristics required in thermal nanoimprint lithography processes. Furthermore, besides the commercially offered products every specific film thickness between 50 nm up to 20 microns can be customized. Due to the characteristic solubility behaviour of COC, double or multi-layer coating via spin-coating is additionally possible to achieve even thicker films of 40 µm or even 60 µm. In the following literature compilation and selection of scientific papers we will give the reader a broader overview on the overall material characteristics of COC as well as some recent applications in next generation devices underlined by examples using mr-I T85 COC formulations. In addition, we demonstrate the imprint-ability by reviewing different use cases of optical and micro-fluidic applications.

Summary of the Outstanding COC Material Characteristics

- COC is a low-cost and light weight polymer and perfectly suitable as a substitute of glass due to the **exceptional optical transparency** in UV/vis, IR, far-IR, the high Abbe number, low birefringence, great optical stability, and **outstanding low autofluorescence** properties.
- COC shows **good resistance to acids and alkaline solutions as well as polar solvents** like alcohols. In contrast, contact to non-polar solvents like aliphatic, aromatics, oils or gasoline should be avoided.
- COC is an **excellent insulator with extremely low dielectric constant** of 2.35 and dielectric loss of 2.02 at 60 Hz (lower than standard BCB). In addition, the very **good metallization characteristics** where no additional adhesion promoters or primers are needed make COCs attractive for electronic high frequency applications.
- The **low moisture absorption potential** makes COC extremely interesting as water barrier thin film. In addition, COC shows a comparatively low nitrogen and air permeability compared to other more generic thermoplastic polymers.
- Almost no detectable extractables are the basic key for the **excellent biocompatibility and low cytotoxicity** of COCs. Furthermore, the stability towards gamma and electron radiation and the resistance to dimethyl sulfoxide (DMSO) makes COC perfectly usable for micro-fluidic and diagnostic life-science devices. The high UV and near UV light transmission properties as well as the low autofluorescence allow low signal to noise ratios for spectrometer readouts.
- COC shows **exceptional mechanical strength** and great compatibility to diverse standard industrial manufacturing processes. In combination with the optical parameters COC is perfectly suitable for optical components requiring high precision.
- The distinct solubility characteristics of COC in non-polar organic solvents compared to many other common polymers or materials which are used for lithographic processes which usually show good solubility in polar organic solvents renders the **realization of bilayer-applications** without the risk of intermixing.
- COC can undergo different ways of subsequent processing steps: It shows a **dry etch performance comparable to standard photoresists** (e.g. SU-8) for pattern transfer via reactive ion etching (see Fig. 3). COC shows a **very good adhesion to metals** like aluminum, chromium, or silver, deposited via vacuum deposition methods and can be directly metallized without additional pretreatment. Furthermore, the surface of COC can be modified with e.g. SiO_2 or TiO_2 deposited via physical vapor deposition (PVD).

Table 1. Intrinsic material characteristics make COC useful for various applications.

Material characteristic	Potential application scenario
Glass-like transparency, low chromatic aberration, low birefringence, and high Abbe number, low autofluorescence	Optical lenses, optical sensors
Extremely low water absorption and permeability	Microfluidic applications, optical sensor applications, electronic devices
Resists acids, bases, and polar solvents	Microfluidic applications
Excellent insulator with extremely low dielectric loss	Electronic devices
Replicates submicron surface features	Microfluidic applications, optical sensor applications, electronic devices
Good metallization characteristics, no adhesion promoter required	Optical sensor applications, electronic devices

CONCLUSION

With the chemical nature and structure of COC this material class renders a perfect solution for many applications where the special solubility characteristics, mechanical properties, as well as optical, electrical and other physical characteristics like the outstanding low moisture absorption potential cannot be met by more generic polymer classes like PMMA, PS, or PC. Hence, COC is able to pave the way to novel and groundbreaking applications which hardly can be realized by the use of other optical polymers. With the mr-I T85 formulation for thin film manufacturing micro resist technology GmbH provides a technical solution for spin-coating approaches which is proved to be ready for being applied in nanotechnology, micro-fluidic chip and life-science applications, as well as in micro-optical devices. The glass transition temperature of 85 °C may actually limit the application scenarios of mr-I T85, but micro resist technology GmbH is developing thin film formulations for material deposition via spin-coating processes with higher glass transition temperatures. With these new products for high temperature applications we will give our customers more options and more freedom to operate for engineering next generation devices.

ACKNOWLEDGEMENT
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APPENDIX: APPLICATION EXAMPLES OF MR-I T85 (COC)

1. Microfluidic device with integrated laser and optical lenses

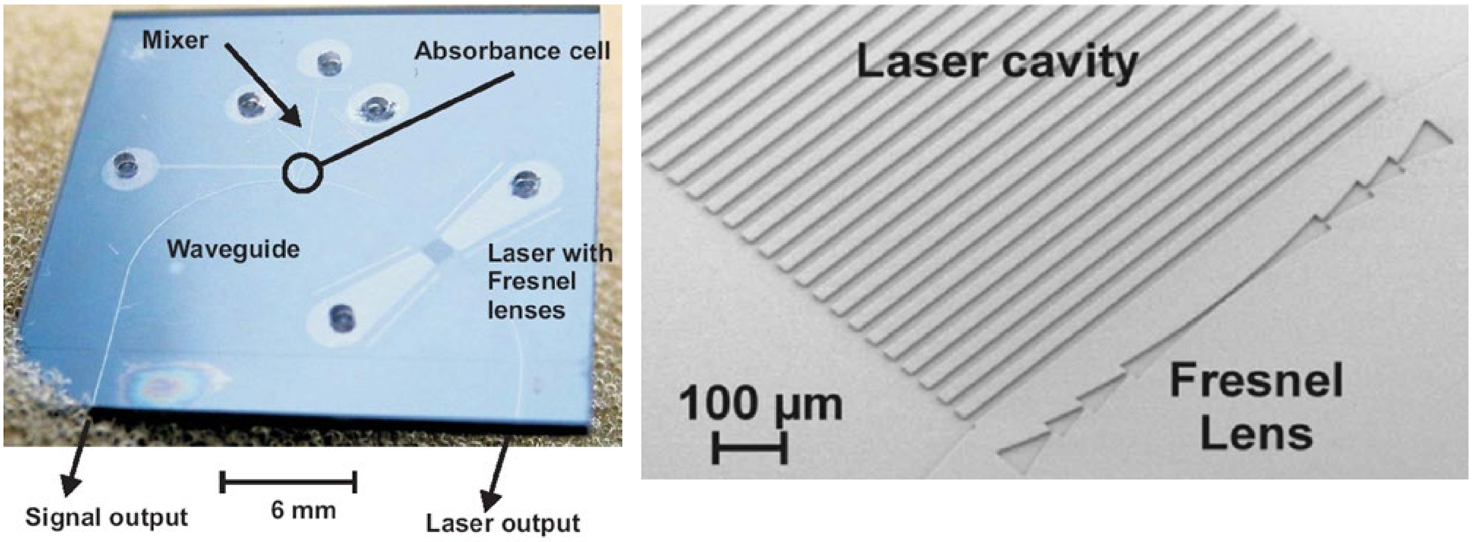

Fig. 3. Microfluidic device imprinted into mr-I T85 with integrated laser cavity and Fresnel lenses (left: photo of the microfluidic chip; right: SEM image of the imprinted laser cavity and Fresnel lens in mr-I T85 thin COC film; courtesy of DTU).

2. Typical process flow for the realization of e.g. microfluidic devices using spin-coated COC thin films and thermal nanoimprint lithography (T-NIL) for mass fabrication (for manufacturing details please contact micro resist technology GmbH).

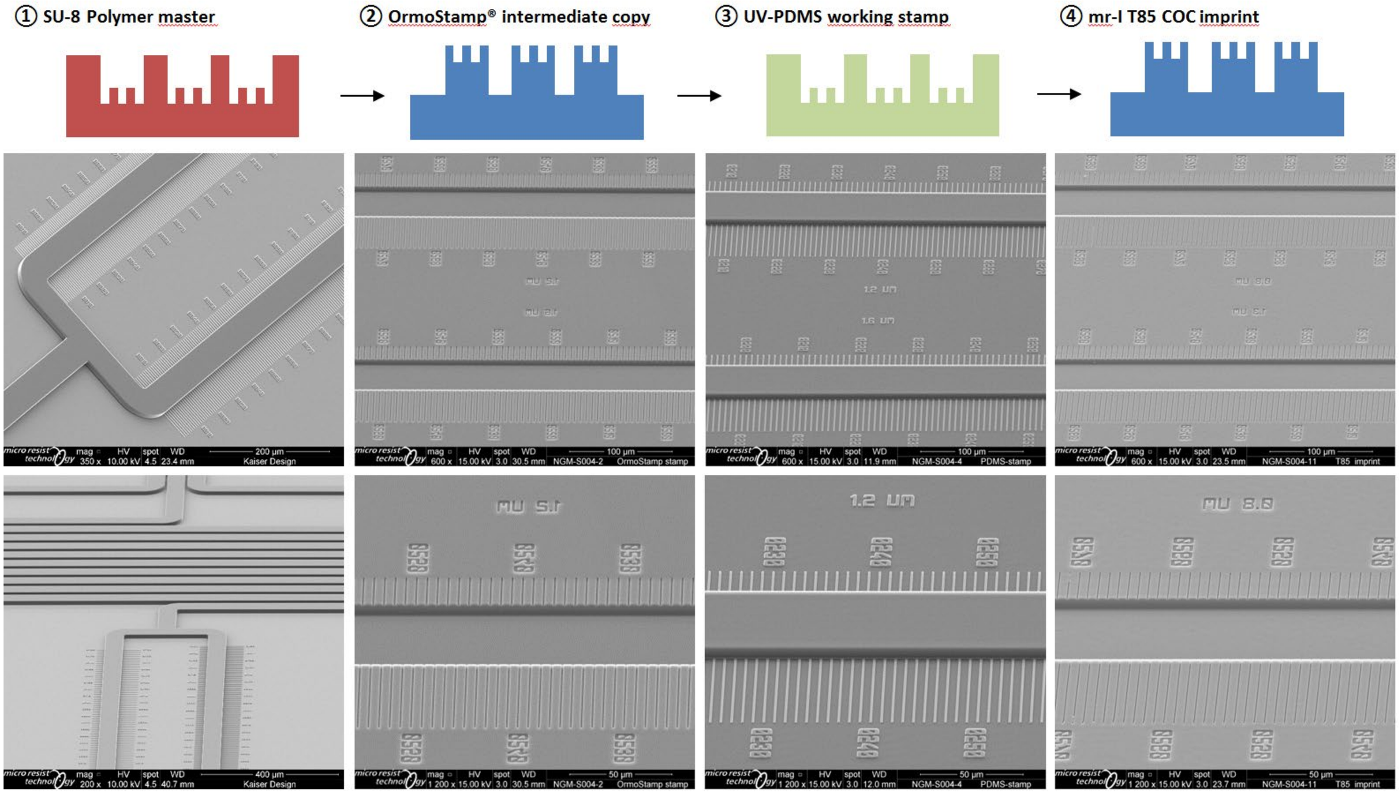

Fig. 4. Typical process flow for the realization of microfluidic devices with mr-I T85 spin-coated thin films (upper row), including SEM images of each single process step (lower row). The exemplary process demonstrates an easy and repeatable manufacturing route for the "mother machine", developed by Wang.[1] Outer left: standard negative type photolithography process with SU-8 negative tone photoresist and wet chemical development for polymer master fabrication (1); Middle left: fabrication of an intermediate copy of the master using OrmoStamp® (2); Middle right: manufacturing of a soft working stamp using UV-PDMS KER-4690 (3); Outer right: final imprint into mr-I T85 COC thin film on silicon wafer (4).

3. Photonic crystal waveguide filter fabricated with T-NIL and etched via RIE into silicon

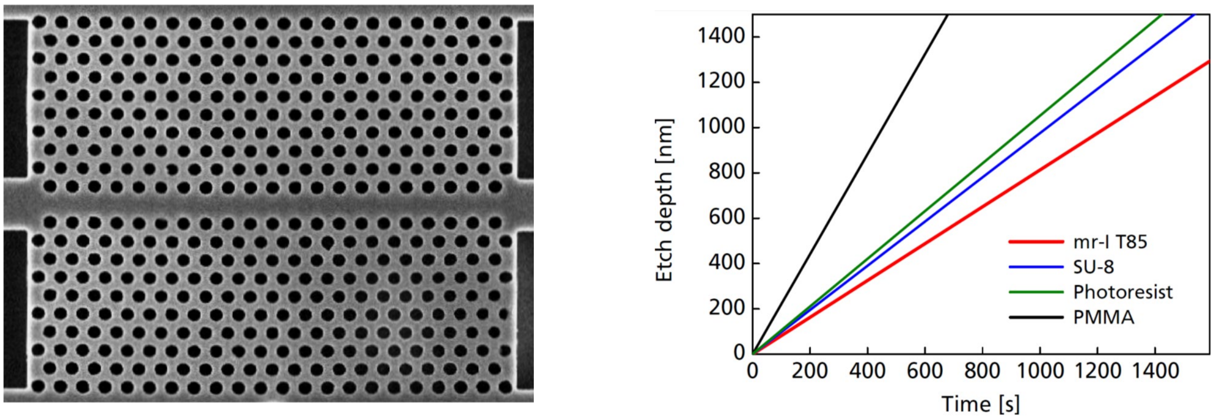

Fig. 5. Photonic crystal wave guide filter etched into Si using spin-coated and imprinted mr-I T85 as etch mask (200 nm diameter holes, 320 nm depth, courtesy of DTU). RIE etch performance of mr-I T85 in comparison to standard photoresists and PMMA.

4. Literature review of fabrication technologies where mr-I T85 is applied as functional material

Table 2. Literature review of fabrication technologies where COC or mr-I T85 is applied as functional thin film material.

Application technology	Manuscript title	Journal source (DOI)
Micromachining	Micromachining Microchannels on Cyclic Olefin Copolymer (COC) Substrates with the Taguchi Method [2]	10.3390/mi8090264
	Micro Lasers by Scalable Lithography of Metal-Halide Perovskites [3]	10.1002/admt.201800212
Nanoimprint Lithography (NIL)	Thermal nanoimprint lithography for drift correction in super-resolution fluorescence microscopy [4]	10.1364/OE.26.001670
NIL with pattern etch transfer	Nanoimprint Lithography of Topology Optimized Photonic Crystal Devices [5]	10.1109/CLEO.2006.4628228
	Imprinted silicon-based nanophotonics [6]	10.1364/OE.15.001261
	Fabrication of ultrathin suspended polymer membranes as supports for serial protein crystallography [7]	10.1016/j.mne.2020.100053
Double layer NIL	Double-Layer Imprint Lithography on Wafers and Foils from the Submicrometer to the Millimeter Scale [8]	10.1021/am101187n
Hot embossing	Microfluidic applications, optical sensor applications, electronic devices [9]	10.1007/s00542-011-1366-z
Working stamp for NIL, µC-Printing, or other lithographic techniques	High-Resolution Contact Printing with Chemically Patterned Flat Stamps Fabricated by Nanoimprint Lithography [10]	10.1002/adma.200803809
	Large-Area Nanoscale Patterning of Functional Materials by Nanomolding in Capillaries [11]	10.1002/adfm.201000492
	Conductive polymer nanowire gas sensor fabricated by nanoscale soft lithography [12]	10.1088/1361-6528/aa905b
	Chemiresistive Sensor Array from Conductive Polymer Nanowires Fabricated by Nanoscale Soft Lithography [13]	10.1039/C8NR04198A
	Graphene Oxide Doped Conducting Polymer Nanowires Fabricated by Soft Lithography for Gas Sensing Applications [14]	10.1109/JSEN.2018.2833146
	A Fully Integrated Wireless Flexible Ammonia Sensor Fabricated by Soft Nano-Lithography [15]	0.1021/acssensors.8b01690
	Rapid response flexible humidity sensor for respiration monitoring using nano-confined strategy [16]	10.1088/1361-6528/ab5cda

5. Literature review of devices where mr-I T85 is applied as functional material

Table 3. Literature review of devices where COC or mr-I T85 is applied as functional thin film material.

Application technology	Manuscript title	Journal source (DOI)
BioMEMS	Surface functionalization of cyclic olefin copolymer (COC) with evaporated TiO_2 thin film [17]	10.1016/j.apsusc.2015.11.234
	Versatile surface functionalization of cyclic olefincopolymer (COC) with sputtered SiO_2 thin film for potential BioMEMS applications [18]	10.1039/B904663A

Application technology	Manuscript title	Journal source (DOI)
Terahertz electronics and optical filters	Development and characterization of cyclic olefin copolymer thin films and their dielectric characteristics as CPW substrate by means of Terahertz Time Domain Spectroscopy [19]	10.1016/j.mee.2018.01.036
	Broadband ultra-low-loss mesh filters on flexible cyclic olefin copolymer films for terahertz applications [20]	10.1063/1.4798522
	Terahertz filter integrated with a subwavelength structured antireflection coating [21]	10.1063/1.4939571
	A terahertz in-line polarization converter based on through via connected double layer slot structures [22]	10.1038/srep42952
	Broadband Terahertz Circular-Polarization Beam Splitter [23]	10.1002/adom.201700852
	Metallic and Dielectric Resonators in Broadband Half-Wave Mirrors for Terahertz Frequencies [24]	10.1109/AUSMS.2018.8346967
	High-Q Terahertz Absorber with Stable Angular Response [25]	10.1109/TTHZ.2020.2964812
	Ultra-wideband tri-layer transmissive linear polarization converter for terahertz waves [26]	10.1063/1.5144115
Dielectric material	Dielectric material for metal/dielectric-coated hollow glass waveguides (HGWs) in infrared lasers [27]	10.1364/AO.54.009548
	Terahertz Reflectarray with Enhanced Bandwidth [28]	10.1002/adom.201900791
Thin film electret membranes	Charge storage and mechanical properties of porous PTFE and composite PTFE/COC electrets [29]	10.1515/epoly.2010.10.1.326
	Electret-material enhanced triboelectric energy harvesting from air flow for self-powered wireless temperature sensor network [30]	10.1016/j.sna.2017.12.067
Optical material	Far-infrared properties of cyclic olefin copolymer [31]	10.1364/OL.384430
Perovskite lasers	Micro Lasers by Scalable Lithography of Metal-Halide Perovskites [3]	10.1002/admt.201800212
Thin film capacitors	Olefin Multilayer Film And Film Capacitor [32]	Patent WO 2017/022706
Microfluidics	Pinched flow fractionation devices for detection of single nucleotide polymorphisms [33]	10.1039/b802268b
	Micro fabrication of cyclic olefin copolymer (COC) based microfluidic devices [9]	10.1007/s00542-011-1366-z
Optical waveguide	Nanoimprinted reflecting gratings for long-range surface plasmon polaritons [34]	10.1016/j.mee.2007.01.110
Bio-applications	Thermal nanoimprint lithography for drift correction in super-resolution fluorescence microscopy [4]	10.1364/OE.26.001670
Gas sensor applications	Graphene Oxide Doped Conducting Polymer Nanowires Fabricated by Soft Lithography for Gas Sensing Applications [14]	10.1109/JSEN.2018.2833146
Graphene release agent	A Universal Stamping Method of Graphene Transfer for Conducting Flexible and Transparent Polymers [35]	10.1038/s41598-019-40408-w
COC Membranes	Fabrication of ultrathin suspended polymer membranes as supports for serial protein crystallography [7]	10.1016/j.mne.2020.100053
Sub-diffraction-limited optical imaging	Thin film Ag superlens towards lab-on-a-chip integration [36]	10.1364/OE.17.022543
	Experimental Investigation of Fang's Ag Superlens suitable for Integration [37]	10.1117/12.82594
	High Aspect Subdiffraction-Limit Photolithography via a Silver Superlens [38]	10.1021/nl2044088

TECHNICAL APPENDIX

Film thickness of different mr-I T85 formulations in dependence of the spinning speed during spin-coating (30 sec. spin time)

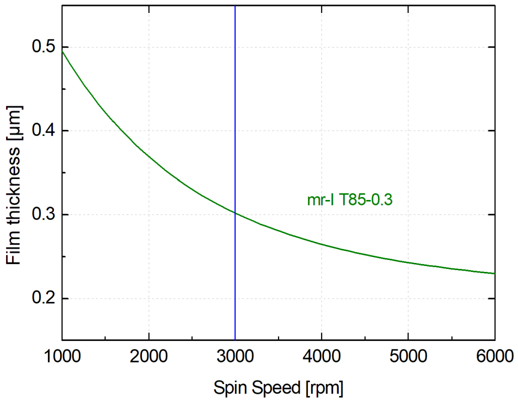

Fig. 6. Spin curve mr-I T85-0.3

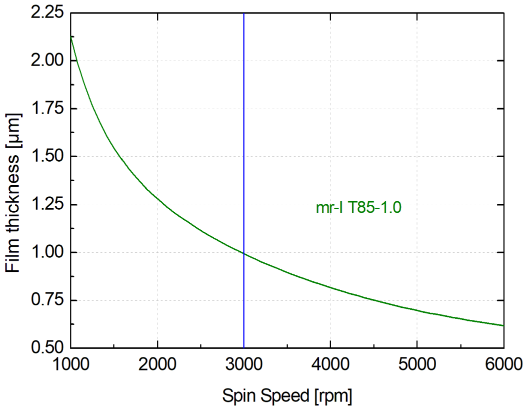

Fig. 7. Spin curve mr-I T85-1.0

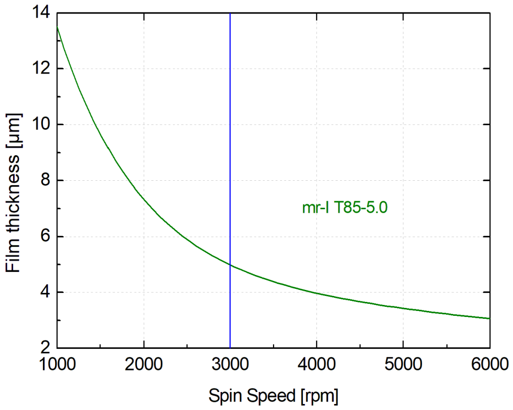

Fig. 8. Spin curve mr-I T85-5.0

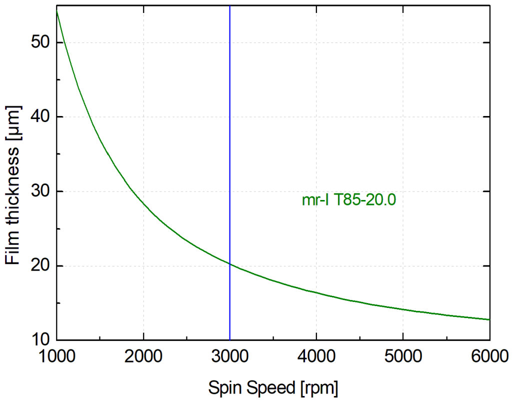

Fig. 9. Spin curve mr-I T85-2µm_XP

Optical properties of mr-I T85 COC polymer after spin-coating and soft bake

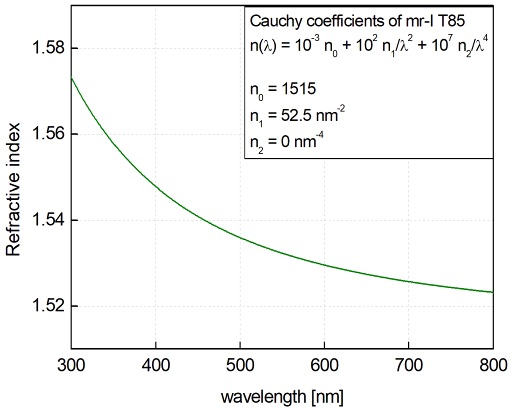

Fig. 10. Refractive index vs. wavelength, inset: Cauchy coefficients of mr-I T85

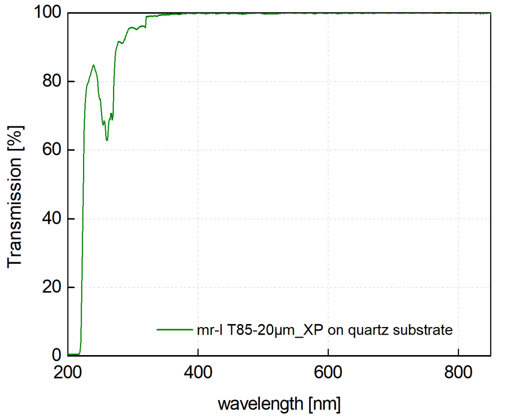

Fig. 11. UV/vis-Transmission properties of mr-I T85 as 20 micron thin film of quarz

[1] P. Wang et al., Curr. Biol. 20 2010 1099
[2] P.-C. Chen et al., Micromachines 8 2017 264
[3] O. Bar-On et al., Adv. Mater. Technol. 2018 1800212
[4] Y. Youn et al., Optics Express 26 2018 1670
[5] B. Bilenberg et al., 2006 Conference on Lasers and Electro-Optics and 2006 Quantum Electronics and Laser Science Confe[1]rence, Long Beach, CA, USA, 2006
[6] P.I. Borel et al., Optics Express 3 2007 1261
[7] A. Karpik et al., Micro Nano Eng. 7 2020 100053
[8] P.F. Moonen et al., ACS Appl. Mater. Interfaces 3 2011 1041
[9] R.K. Jena, C.Y. Yue, Y.C. Lam, Microsyst. Technol. 18 2012 159
[10] X. Duan et al., Adv. Mater. 21 2009 2798
[11] X. Duan et al., Adv. Funct. Mater. 20 2010 2519
[12] N. Tang et al., Nanotechnology 28 2017 485301
[13] Y. Jiang et al., Nanoscale 10 2018 20578
[14] N. Tang et al., IEEE Sensors Journal 18 2018 7765
[15] N. Tang et al., ACS Sens. 4 2019 726
[16] C. Zhou et al., Nanotechnology 31 2020 125302
[17] L. El Fissi et al., Appl. Surface Sci. 15 2016 670
[18] K.-S. Ma et al., J. Mater. Chem. 19 2009 7914
[19] L.M. Diaz-Albarran et al., Microelctron. Eng. 911 2018 84
[20] F. Pavanello et al., Appl. Phys. Lett. 102 2013 111114
[21] J.M. Woo et al., AIP Advances 5 2015 127238
[22] J.M. Woo, S. Hussain, J.-H. Jang, nature Scientific Reports 7 2017 42952
[23] W.S.L. Lee et al., Adv. Optical Mater. 2017 1700852
[24] W.S.L. Lee et al., Australian Microwave Symposium AMS 2018
[25] A. Ebrahimi et al., IEEE Transactions on Terahertz Science and Technology 10 2019 204
[26] R.T. Ako et al., APL Photon 5 2020 046101
[27] J.E. Melzer and J.A. Harrington, Applied Optics 54 2015 9548
[28] X. You et al., Adv. Optical Mater. 2019 1900791
[29] W.C. Koo et al., e-Polymers 2010 32
[30] Y. Wu et al., Sensors and Actuators A: Physical 271 2018 364
[31] E.J. Wollack et al., Optics Letters 45 2020 780
[32] Y. Imanishi, M. Ohkura, K. Okada, Patent WO 2017/022706
[33] A.V. Larsen et al., Lab Chip 8 2008 818
[34] R.H. Pedersen et al., Microelectron. Eng. 84 2007 895
[35] B.N. Chandrashekar et al., nature Scientific Reports 9 2019 3999
[36] C. Jeppesen et al., OPTICS EXPRESS 17 2009 22548
[37] C. Jeppesen et al., Proc. of SPIE 7395 2009 73951I-1
[38] H. Liu et al., Nano Lett. 12 2012 1549