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Hybrid polymers processed by substrate conformal imprint lithography for the fabrication of planar Bragg gratings

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Abstract In this work, we present an approach to use UV-enhanced substrate conformal imprint lithography (UV-SCIL) as a soft imprint technique combined with excimer laser irradiation to manufacture Bragg gratings within planar waveguides on a full-wafer scale. For the first time, different hybrid polymers (OrmoComp®, OrmoStamp, OrmoCore, OrmoClad and OrmoClear) could be successfully patterned using UV-SCIL. For OrmoComp® (showing results very similar to OrmoStamp and OrmoClad), a complete imprint process could be realized. OrmoCore formed an inhibition layer in the presence of oxygen during the imprint, as could be observed for the use of OrmoClear as well. Processing options were elaborated to reduce the inhibition effect significantly, whereby the latter is mainly due to the atmospheric oxygen-containing PDMS layer of the UV-SCIL working stamp. Further on, the successful realization of a planar Bragg grating operating at the telecom wavelength is demonstrated by tuning the refractive index (RI) of OrmoComp® using a phase mask and an UV excimer laser. FTIR measurements show that the change in RI can be clearly correlated with a change in the chemical composition of the hybrid polymer during laser exposure.

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1 Introduction

Optical sensor devices using waveguide structures have gained a lot of interest during the last years. In particular, the fields of chemical analyses or medical applications are becoming more important (e.g., in lab-on-a-chip systems) including systems with several sensor elements, couplers and waveguides integrated on a single chip [1]. As the required structural dimensions often have to be below 1 μm, the corresponding manufacturing technique needs to be able to resolve structures in the nanometer regime. Silicon dioxide is a common material for the fabrication of waveguides, but has the disadvantage of expensive and time-consuming processing [1]. Other solutions suggest organic polymers due to their ability to be structured with cost-effective imprint techniques. However, high optical losses as well as low chemical and physical stability limit their area of application [2]. Therefore, alternative materials and innovative manufacturing processes have to be found. Hybrid polymers might be a material alternative because this material class combines the positive characteristics of inorganic materials (physical and chemical stability) and organic materials (simple molding, UV-curing) [3]. By changing the composition of organic and inorganic components, one can increase the thermal stability of hybrid polymers up to 400 °C and change their Young's modulus from 0.013 GPa up to 18.6 GPa according to the preferred application [3]. In particular, the tunable refractive index (ranging from 1.42–1.65) [3] makes the material class very interesting for a broad field of optical applications.

As presented in different publications (e.g., [4–6]), hybrid polymers can be successfully patterned using nanoimprint lithography. While these works show that requirements regarding aspect ratio, dimension and surface quality of imprinted structures can be successfully fulfilled using already approved techniques combined with hybrid polymers, the limitation of the imprint area is not solved, yet. UV-enhanced substrate conformal imprint lithography [7, 8] could be an innovative and cost-effective solution to pattern hybrid polymers. This technology uses flexible polydimethylsiloxane (PDMS) stamps to pattern substrates up to 200 mm diameter with features down to a size of a few nanometers [8]. For the transfer of nanometer structures into the imprint resist, the standard method uses a three-layer stamp concept [7]. Such stamps are composed of a thin glass back plate (200 µm thickness), a soft PDMS (S-PDMS) buffer layer (600 µm thickness) and a structure containing layer (100 µm thickness) made of special PDMS with a high Young's modulus [8]. Furthermore, distortions of the structures during the imprint process are avoided by using only a small imprint pressure (20 mbar) and mainly capillary forces to pull the stamp into the resist layer [8].

Fast and reliable imprint processes using epoxy-based resists have shown the potential of UV-SCIL for industrial manufacturing processes [9], strengthened by studies on stamp lifetime [10] and accuracy of the structure transfer [7]. Investigations on the UV-SCIL suitability for optical applications also have shown promising results [11]. Using this imprint technique in combination with UV-curable hybrid polymers, three-dimensional photonic structures including, e.g., sensor elements, waveguides and couplers can, in principle, be molded with one single imprint step and as one piece while benefiting from the material characteristics of hybrid polymers. Thus, the number of optical transitions can be significantly reduced resulting in decreased attenuation and transfer losses. Such an optical device could be a Bragg grating sensor [12]. The field of application for such sensors includes temperature, pressure and strain sensing [12] or chemical analyses [13, 14]. Previous works using conventional PMMA instead of hybrid polymers already proved that a change of the refractive index can be achieved by excimer laser irradiation of the polymer [15]. Confirming these investigations using hybrid polymers would be an important step toward fabricating planar Bragg gratings in imprinted hybrid polymer waveguides benefiting from enhanced material properties compared to conventional polymers.

Within this work, it could be shown that the investigated hybrid polymers are compatible with the UV-SCIL technology. Waveguiding structures could be imprinted on a wafer scale up to 150 mm in diameter. Planar Bragg gratings could be realized and successfully tested using hybrid polymer waveguide structures by periodically modifying the polymer's refractive index.

2 Experimental

Two different silicon wafers with periodic waveguide structures were produced using mask aligner lithography and reactive ion etching (Layout A and B). The wafers served as masters for molding the PDMS stamps which are applied for UV-SCIL. Layout A is designed to investigate the UV-SCIL compatibility of the hybrid polymers, whereas Layout B is designed to fabricate waveguides used for investigations on the optical properties of the hybrid polymers.

The waveguide structures of Layout A have a height of around 10.4 µm and a width of 7.4 µm. Neighboring structures are separated by a 150-µm-wide mesa structure (see Fig. 1). These mesa structures are supposed to trap potential defects or air inclusions. They have no functionality for potential optical investigations.

Regarding Layout B, the design consists of several arrays of waveguides. For each of those arrays, the width of the waveguides is varied from 7 to 21 µm in steps of 2 µm in order to investigate the correlation between size and optical behavior of the waveguides. Single waveguides are separated by a pitch of 100 µm. The height of the structures was determined to be 9.8 µm, measuring their cross section at a cleaved edge with a secondary electron microscope (SEM, JEOL JSM 7610F). Top-view images of imprinted structures were taken with the SEM of a FEI Helios Nanolab 600. In order to achieve smooth sidewalls, a continuous etching process was chosen for the master fabrication, providing a higher surface quality and therefore lower optical losses in the imprinted polymer

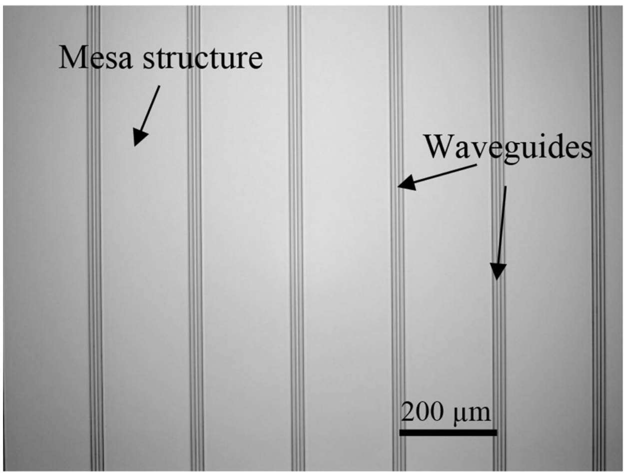

Fig. 1 Top-view image of imprinted waveguides (Layout A, OrmoComp®) observed through an optical microscope at ×100 magnification

waveguides [16]. No mesa structures are contained in between the waveguides.

Before the molding of the PDMS stamps, the master wafers were coated with an anti-sticking layer consisting of FDTS (perfluorodecyltrichlorosilane) using molecular vapor deposition (MVD). Since only structures in the micrometer regime were to be transferred during this investigation, the stamp was only manufactured with a single S-PDMS layer (Sylgard 184) as the pattern-containing layer [7].

For the imprint process, different hybrid polymers (OrmoComp®, OrmoCore, OrmoStamp, OrmoClear, OrmoClad, from *micro resist technology* GmbH, Germany) were spin coated on 100-mm or 150-mm Si wafers. All imprints were performed on a MA/BA8 mask aligner from SUSS MicroTec equipped with the SCIL tooling (UV intensity: 37 mW/cm^2 at 365 nm). To ensure that the hybrid polymers were fully cured, an exposure dose of 2400 mJ/cm^2 was applied during every imprint. After the UV-curing, an additional hardbake was performed on a hotplate for 120 s at 90 °C. The resulting dimensions of the imprints were analyzed and compared with the master structures with a SEM (JEOL JSM 7610F).

All stamps and, thus, all waveguides used for the Bragg grating studies were replicated from Layout B.

The grating was written into the material via UV excimer laser radiation (248 nm, 16,000 mJ/cm^2, 100 Hz) using an Ibsen photonic phase shift mask (pitch: 1036 nm; second-order Bragg grating). The expected Bragg wavelength is supposed to be around 1561 nm.

Further on, the functionality of the grating was controlled using an interrogator system from sm125-500 by Micron Optics. The system operates in the telecom wavelength range from 1510 to 1590 nm (resolution 1 pm; sampling rate 2 Hz). The light is guided to the samples via a single-mode glass fiber bonded to the sample using a v-groove fiber array. The reflected spectrum was monitored and analyzed with the included software. The measurements were taken at room temperature under standard conditions.

For further understanding of the chemical processes within the material during laser irradiation, Fourier transform infrared spectroscopy (FTIR) measurements were taken. Samples with unstructured UV-cured layers (30 µm thickness) of OrmoComp® were irradiated with different UV laser fluencies and measured by means of FTIR in order to investigate the UV-induced changes within the hybrid polymer. The fluencies of the 248-nm KrF excimer laser varied from 0 to 100,000 mJ/cm^2. Every prepared sample was measured under identical conditions in a Bruker Vertex 70 FTIR system (64 scans, wavenumber 200–5000 cm^{-1}, apodization: Blackman-Harris-3-term).

3 Results and discussion

Due to the imprint results, the investigated hybrid polymers can be divided into two major groups. The material modifications exhibiting no oxygen inhibition (e.g., OrmoComp®, OrmoStamp and OrmoClad) showed a successful replication of the original structures (in the following, OrmoComp® can be seen as a representative for this group). The second group of materials suffering from oxygen inhibition includes OrmoCore and OrmoClear and will be discussed later on.

With the use of OrmoComp®, optimized imprint process parameters led to fully replicated waveguide structures over a large area as can be seen in Fig. 1. Substrates with dimensions up to 150 mm diameter could be patterned.

Further improvements of the process led to reduced curing times below 60 s. Only few imprint defects could be observed on the imprinted samples which were mainly caused by air inclusions. These air inclusions only occurred in the mesa structures between two waveguides, but did not affect the latter with regard to their structural dimensions. Imprints realized with a different (and for SCIL already evaluated [9]) imprint resist (DELO Katiobond) showed very similar defects. Thus, the air inclusions are likely to be an effect of the structural dimensions and are not caused by the use of OrmoComp® as imprint polymer.

To compare the dimensions of a single waveguide from the original silicon structure with the transferred hybrid polymer, cross-sectional images were taken from both imprint and silicon master and investigated using a SEM (see Fig. 2). The shape of the patterned waveguide corresponds very well to the silicon master structure. An overall shrinkage of the waveguide dimensions of about 7 % was observed during the imprint process. This value is in good agreement with the data provided in the specifications of the resist supplier [17].

Besides the shrinkage, the OrmoComp® structures show no degradation, especially when considering the separation from the stamp. All imprints were separated from the stamp manually. After more than ten imprints with a single stamp, neither the stamp nor the imprint results showed any additional degradation.

The group of oxygen-inhibitant hybrid polymers in the following represented by OrmoCore showed a similar behavior as an imprint polymer for UV-SCIL. However, a residual liquid layer at the contact region to the PDMS stamp remained after the UV-curing step. As the exposure dose of the UV radiation was defined far above the necessary dose, insufficient radiation can be excluded as the cause of this effect. Another possible reason is the oxygen inhibition of OrmoCore. PDMS is permeable for solvents as well as for gases [12], and thus, atmospheric oxygen is

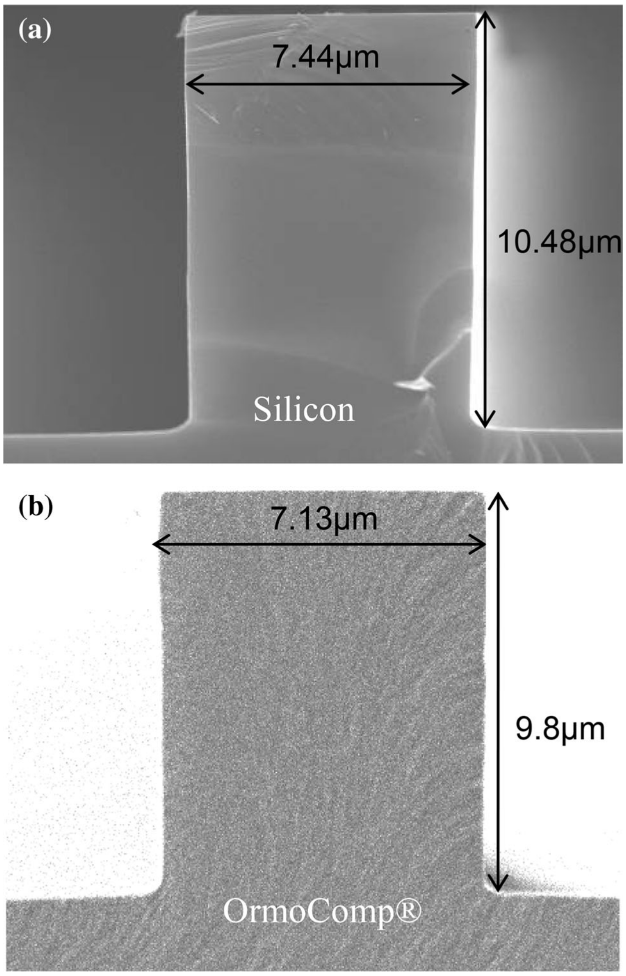

Fig. 2 **a** SEM cross-sectional image of a waveguide structure of the silicon master (Layout A) compared to **b** the cross section of an imprint performed with OrmoComp® after UV-curing and hardbake

present in the stamp during the imprint, which inhibits the curing of OrmoCore at the contact area. The dimension of the inhibition layer can be estimated from Fig. 3. The SEM cross section shows a waveguide after removing the liquid part of OrmoCore using OrmoDev as washing solvent. The remaining structure had a width of 4.5 µm and a height of 8.2 µm, resulting in an average dimensional loss of 30 % compared to the original dimensions. Thus, to achieve an optimum replication of the structures including a high reproducibility while using OrmoCore as an imprint polymer, an adapted process was investigated.

The approach of this alternative treatment was to investigate the effect of a reduced oxygen concentration within the stamp on the imprint results.

Considering this modified imprint process, the only difference compared to the above-mentioned original process was the exposition of the working stamp to a nitrogen atmosphere for more than 14 h before the actual imprint. Thus, the PDMS was supposed to be saturated with nitrogen after leaving the gas chamber. Due to transportation and processing, a partial re-diffusion of oxygen into the PDMS is to be expected right before the imprint itself.

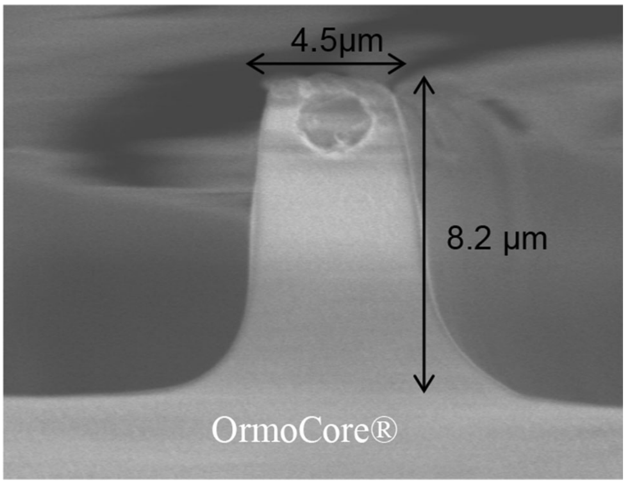

Fig. 3 SEM cross section of an imprint with OrmoCore after UV-curing and removal of the liquid residual layer showing significant dimensional losses and deformation compared to the master structure

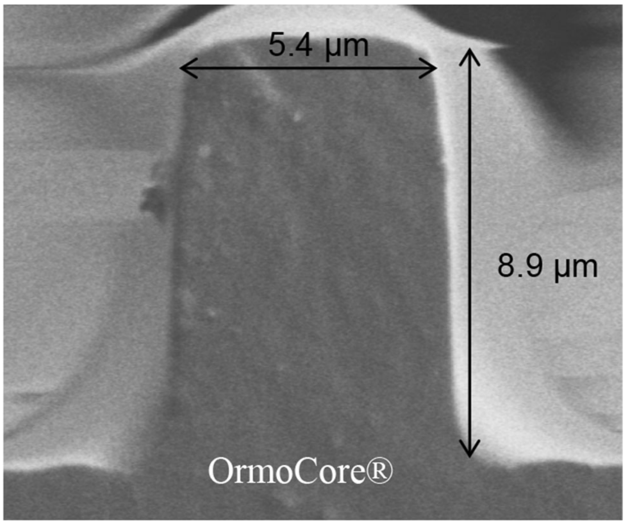

Fig. 4 SEM cross section of an imprint performed with OrmoCore using a nitrogen-purged stamp after removal of the residual liquid layer having a less deformed structure

The result of such an imprint, performed within 2 min after taking the stamp out of the nitrogen atmosphere is shown in Fig. 4. The sample was washed with OrmoDev before taking the pictures. The dimensions of the waveguide (5.4 µm width and 8.9 µm height) compared to those without a previous nitrogen purging (4.5 µm width and 8.2 µm height) show significant improvements regarding the structural dimensions.

The nitrogen treatment of the working stamp, however, is not applicable for a reliable and viable process,

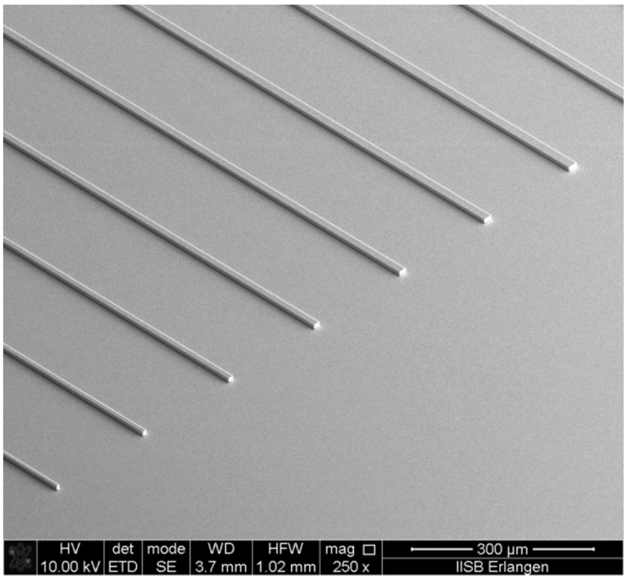

Fig. 5 SEM image of an imprinted waveguide array from Layout B with varying width of the waveguides using OrmoComp® (sample tilted by 52°)

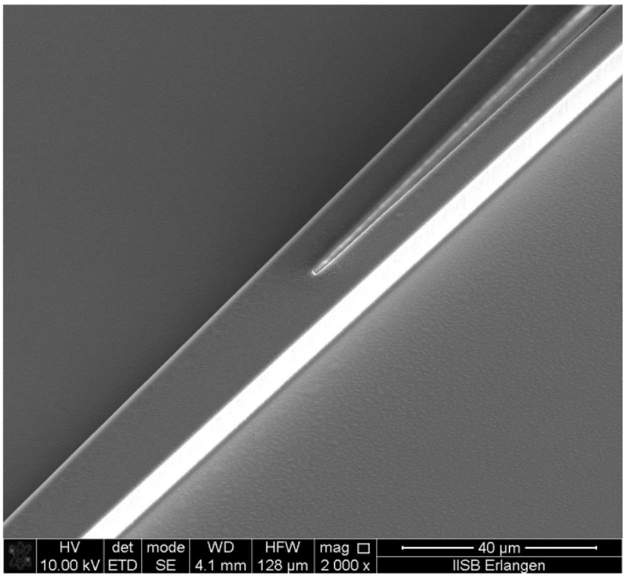

Fig. 6 SEM image of a Y-coupler element (Layout B) imprinted into OrmoComp® (sample tilted by 52°)

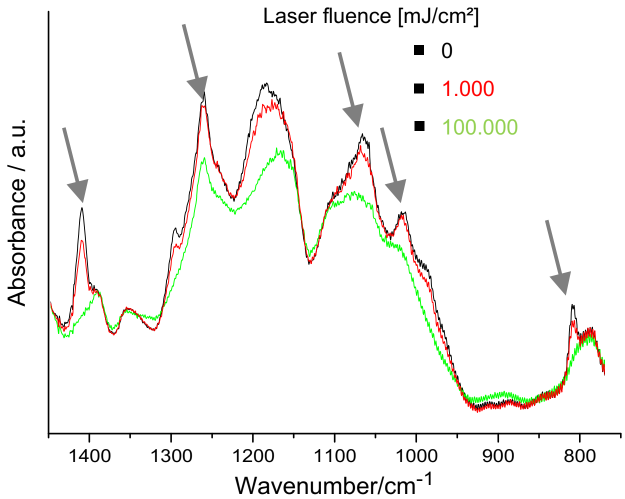

Fig. 7 FTIR spectrum of OrmoComp® samples irradiated with varying laser fluencies. *Arrows* indicate the location of peaks influenced by laser irradiation

especially if several imprints are supposed to be performed in a row. Furthermore, as the described formation of an inhibition layer of OrmoCore could not be excluded completely even with the adapted process, it was decided to produce all waveguides for the following steps exclusively using OrmoComp®.

The investigations regarding the inscription of planar Bragg gratings using UV excimer laser irradiation were performed with waveguides replicated from Layout B using OrmoComp®. Figure 5 shows an array of waveguides imprinted with OrmoComp®, whereas Fig. 6 shows the successful patterning of a more challenging Y-coupling structure.

As described above, UV laser radiation was applied to write planar Bragg gratings into the waveguide. FTIR measurements of OrmoComp® samples confirm that the composition of the hybrid polymer changes during the exposure to UV irradiation. Figure 7 shows a part of a measured FTIR spectrum of samples with OrmoComp® exposed to rising laser fluencies, from zero to 100,000 mJ/cm^2. Several peaks show decreasing amplitudes with rising fluency, which means that chemical bonds are broken up within the material. Thus, the composition and, hence, the optical properties of the hybrid polymer are changed by the laser irradiation.

The surface of a hybrid polymer was investigated after exposition to UV light with a fluency of 96,000 mJ/cm^2. That is six times the fluency used for the actual creation of the functional Bragg gratings. A little change in the surface topography can be seen as a side effect of the chemical process or the laser treatment. It almost disappears for the lower fluency (16,000 mJ/cm^2) used for the creation of functional gratings.

The functionality of the Bragg grating written into OrmoComp® was confirmed by measuring a Bragg reflection. Subsequently, this proofs a change of the refractive index within the material by the use of excimer laser irradiation. Figure 8 shows the resulting peak measured by the interrogator system, as described in the experimental part. The Bragg peak is found to be at a wavelength of 1564 nm for the performed measurement. The theoretical Bragg wavelength λ_B is determined by the equation:

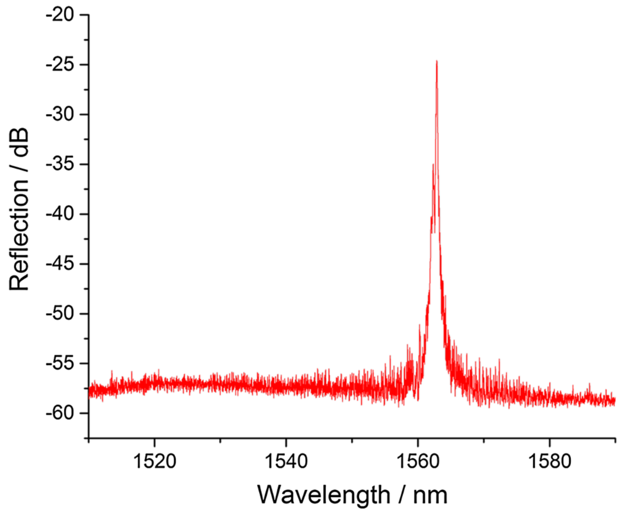

Fig. 8 Extract of the reflected spectrum of a Bragg grating written into OrmoComp® showing a maximum at 1564 nm

$$m\lambda_B = 2n_{eff}\Lambda$$

where Λ is the grating period, n_{eff} the modal effective refractive index and m is the refraction order of the grating. The expected Bragg wavelength (1561 nm) is in very good agreement with the measured peak (1564 nm).

Overall, the reflected spectrum proofs the presence of a Bragg grating, written into a planar waveguide manufactured by UV-SCIL out of OrmoComp®.

4 Conclusions

This work shows, for the first time, the successful use of UV-SCIL in combination with hybrid polymers (OrmoComp®, OrmoCore, OrmoStamp, OrmoClear, and OrmoClad). Planar waveguides could be fabricated on wafer scale (up to 150 mm). Reproducible patterning results could also be obtained for complex structures like Y-junctions. As a consequence, the combination of material and technology shows high potential for the fabrication of optical devices.

Furthermore, a planar Bragg grating was written into a hybrid polymer by UV excimer laser irradiation using a phase mask. This approach makes it possible to easily integrate sensing devices into the imprinted waveguide structures. Optical measurements showing a clear Bragg reflection serve as a proof of concept for future applications.

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