Inorganic–Organic Hybrid Polymers for Information Technology: from Planar Technology to 3D Nanostructures**

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Sol-gel synthesis allows inorganic–organic hybrid polymer materials (ORMOCER®s) to be produced, which can be functionalized to tailor their physical and chemical properties such as refractive index or optical loss. A particular material system is discussed here, which is synthesized without addition of water and is applied in optical communications. As examples for 2D and 2.5D technology, planar waveguides, stacked waveguides, and microlenses are shown. Using two-photon polymerization initiated by femtosecond laser pulses, arbitrary 3D structures can be made in the submicrometer range. In particular, 3D photonic crystal structures are described and discussed.

1. Introduction

Over the last decade, silicate-based inorganic–organic hybrid polymers (e.g., ORMOCER®) have attracted interest because of the physical and chemical properties resulting from their hybrid nature.[1,2] ORMOCER®s are synthesized by sol-gel processing which offers flexibility in polymer synthesis by variation of the catalysts, temperature, and alkoxyisilane scaffold. This flexibility enables one to tailor their properties to the application.[3,4] Specially synthesized ORMOCER®s are used in optical connections or waveguides, micro-optics, and electro-optical applications.[5] The refractive index can be tuned over a wide range by mixing various resins.[6]

In sol-gel processing, an inorganic-organic network is formed where the inorganic units are functionalized by organic groups. Alkoxyisilanes are used as precursors to build up organically modified inorganic-oxidic nanoscale oligomers of 0.7–10 nm in diameter.[7,8] The organic polymerizable units are typically methacryl, allyl, or epoxy groups,[1,4] which account for the negative resist behavior of the ORMOCER®s. They can therefore be patterned by ultraviolet (UV) irradiation after addition of a suitable UV initiator, which makes them attractive for any kind of wafer-scale applications. ORMOCER®s adhere very well to most substrates such as (metallized) Si wafers, inorganic glasses, and

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other organic polymers. They are stable up to about 355 °C in an oxygen atmosphere and 415 °C in nitrogen.\textsuperscript{[4]}

2. Material Properties

ORMOCER\textsuperscript{®} coatings are usually prepared by hydrolysis/polycondensation reactions (sol-gel processing) from alkoxysilane precursors, followed by an organic cross-linking of the inorganic-oxide units by organically polymerizable groups. These coatings are amorphous and optically transparent. An advantage of ORMOCER\textsuperscript{®} is that their physical properties can be tuned by molecular design of the silane precursors as well as by the sol-gel processing conditions. To account for low optical losses at data and telecom wavelengths (810, 1310, and 1550 nm, respectively) strongly absorbing chemical groups should be avoided in the resulting materials. For example, O–H groups (also derived from water), C–H, and C=O lead to overtone absorption\textsuperscript{[8]} and so have to be avoided.

Figure 1 shows an example of an ORMOCER\textsuperscript{®} system (ORMOCER\textsuperscript{®} I) that was developed for waveguide applications. The synthesis is carried out using a two-component system consisting of 3-methacryloxypropyltrimethoxysilane (MEMO-NT) and diphenylsilanediol (DPD). To avoid absorbing components in the resulting material, a modified sol-gel process is used for this particular synthesis where the Si–O–Si network is established solely by polycondensation reactions without releasing water. The absence of O–H was confirmed by infrared (IR) measurements (not shown) in the range $\tilde{\nu} = 3600–3200$ cm\textsuperscript{-1}.

For this particular ORMOCER\textsuperscript{®}, the nanometer-sized inorganic-oxide units are organically functionalized by methacryl groups, which enable the material to be patterned by UV. Methanol (generated during polycondensation) is removed with a rotational evaporator. This enables a wide range of film thicknesses (up to 150 μm) to be produced, as the resin can be used with or without dilution. For example, to produce single-mode waveguides of about 5 μm thickness, the resin is diluted with propylacetate or 1,2-propandiolmonooethyl ether acetate (which is a propylene glycol methyl ether acetate, PGMEA) leading to a lacquer. The resin is stable for more than one year at room temperature, and even longer if it is stored at lower temperature (–18 °C). The most prominent features of this ORMOCER\textsuperscript{®} are its low optical losses at data and telecom wavelengths, its tunable refractive index, and the high thermal and mechanical stability.\textsuperscript{[10]} Thermal stability (up to 270 °C, < 5 % mass loss) was determined by thermogravimetry-differential thermal analysis (TG-DTA) measurements in the range 50–500 °C, with an annealing rate of 5 K/min under ambient conditions.

3. Experiments, Results, and Discussions

Figure 2 shows the absorption spectrum of a methacrylic cross-linked polycondensate of MEMO-NT with DPD (ORMOCER\textsuperscript{®} I); the synthesis was carried out as discussed previously.\textsuperscript{[11]} The high absorption in the UV (Fig. 2a) is mainly caused by the phenyl groups, which might be probably also responsible for the low optical losses at 1310 nm (0.22 dB/cm) and 1550 nm (around 0.55 dB/cm) (Fig. 2b). Besides the possibility of organically cross-linking the modified inorganic-oxide units by UV irradiation, organic cross-linking can also be initiated by two-photon absorption, which requires low absorption losses at around 780 nm.\textsuperscript{[12]}

Therefore, the processing of the ORMOCER\textsuperscript{®} can be carried out by either UV lithography, combined lithography/reproduction techniques, or two-photon polymerization (2PP) initiated by femtosecond laser pulses. As substrates, Si wafers or glass plates were used. As UV initiator, 1 wt.-% Irgacure 369 was used, which has its absorption maximum at about 340 nm. Typically, the material is spin-coated onto the substrates, but for the combined technology (UV lithography/reproduction) or for 2PP the ORMOCER\textsuperscript{®} is dispensed on the substrates.

For UV lithography, the samples were thermally pre-treated (80 °C/min) on a hotplate subsequently to the coating. After this procedure, the samples were immediately exposed to UV light ($\lambda = 365$ nm) in a conventional mask aligner (energy density about 500 mJ/cm\textsuperscript{2}). Then, the sam-

![Fig. 1. Sketch of the synthesis of ORMOCER\textsuperscript{®} I for waveguide applications.](image)

![Fig. 2. Absorption spectrum of ORMOCER\textsuperscript{®} I resin (with 1 wt.-% Irgacure 369 added): a) before and b) after UV curing. The material clearly shows low absorption for particular wavelengths in the VIS and NIR.](image)
amples were again thermally treated on a hotplate (80 °C/min), followed by a short downcooling period. Before the final thermal curing step, which was carried out at 150 °C (3 h), the layers were developed in a mixture of methylisobutylketone (MIBK) and isopropanol (1:1).

Figure 3 shows an example of 2.5D lithography. The basic idea for making a 2.5D vertical integration is to repeat the fabrication methods already established for planar (2D) waveguide structures. The fabrication of planar waveguides follows a simple sequence of spin coating, heating, UV patterning, development, and thermal curing. First, a suitable under-cladding consisting of a mixture of two ORMOCER®s is prepared by spin coating and UV flood-exposure. The viscosity of the hybrid polymer resin is controlled by dilution with a solvent, which makes it possible to adjust the layer thickness of the respective structures precisely. The core material is spun directly without any further planarization treatment onto the cladding surface, which is possible due to the very good planarization properties of the ORMOCER®s. After a proximity exposure in a mask aligner, the unexposed material is removed with a solvent. Subsequently, an upper-cladding is spun on top of the waveguide structures.

Figure 3 shows a cross-section through the output facet of a single-mode waveguide stack (4 x 8 array) on a Si/SiO2 substrate. The waveguide cross-section is around 5 μm x 5 μm, and the total stack height is about 90 μm. The vertical distance between the waveguides is 22 μm. It is possible to increase the stack height simply by adding additional planar processed waveguide layers. It should be mentioned, however, that the current physical limit of the technology is given by the wafer bow, which increases with increasing stack height due to thermomechanical stress resulting from organic cross-linking, evaporation of solvents, and differences in the coefficient of thermal expansion (CTE) of the substrate and the ORMOCER®. The wafer bow thus prevents a homogeneous exposure gap over the entire substrate, where the present limit is about six waveguide/cladding layers.

Recently developed mask aligners (Süss Microtech, Germany) make it possible to combine photolithography and UV replication, leading to a potential wafer-scale fabrication of diffractive, refractive, and integrated optical devices directly on pre-fabricated substrates, such as wafers with light emitting diode (LED) or vertical cavity surface emitting laser (VCSEL) structures. For that purpose, a lithography mask has been used, which acts as a conventional aperture mask but, in addition, as a molding tool, because master structures were fabricated under the apertures.

Figure 4 shows an exemplary result of a combined lithography/molding process: replicated microlenses with conic spacer structures on GaAs VCSELs for collimation. The experimental sequence (Fig. 4a) starts with the deposition of the ORMOCER® resin onto the substrate. For the combined lithography/molding process, a conventional lithography mask, which is at first a conventional glass plate with a patterned chromium layer as apertures, has been used. Below all apertures of the mask, concave polymer (polydimethylsiloxane, PDMS) microlenses have been fabricated by molding as the master tools for the following combined lithography step. The mask is then adjusted onto the ORMOCER® droplet and the whole arrangement is subsequently exposed to UV light in a mask aligner (Süss MA6). The shape of the master microlenses was designed such that they focus UV light during the exposure process, leading to free-standing conic structures with high aspect ratios up to 9:1 (Fig. 4b).

The ORMOCER® material in the gaps between the structures (750 μm height, free space required for bonding) was not exposed due to the selective exposure (aperture functionality of mask) and was removed with a solvent after separation of mask and sample. With these structures, the beam divergence of the VCSEL emission could be reduced to less than 1°.

Recently, it has been demonstrated that photochemically sensitive materials such as organic polymers or ORMOCER® can also be polymerized by 2PP when using

Fig. 3. Cross-section through the output facet of a 8 x 4 array of stacked single-mode waveguides.

Fig. 4. Replicated microlenses on GaAs VCSEL structures (pitch 250 μm, height 750 μm) produced with combined technology (UV lithography/replication): a) process flow of combined lithography/molding; b) high aspect-ratio conic structures fabricated by combined lithography/molding in ORMOCER®.
femtosecond laser pulses. One prerequisite is that the materials used are transparent in the near-infrared (NIR) (for the present technology 780 nm). If the laser light is focussed into the volume of the liquid resin, femtosecond laser pulses can initiate 2PP. This technique allows structures to be made with a resolution of better than 200 nm.\(^{[13]}\)

To make real 3D structures, the ORMOCER\(^\text{R}\) resin (no solvents used for dilution is dispensed on the substrates and exposed to Ti:sapphire laser radiation (\(\lambda = 780\) nm, 80 MHz, 80 fs). The laser beam is scanned using an XY galvo scanner within the volume of the ORMOCER\(^\text{R}\). The sample can be moved in the Z direction with a translational stage. For femtosecond laser pulses, the photon density in the focal volume is locally high enough to initiate 2PP of the resin within the focal volume. If the focus is moved in 3D through the resin, the polymerization occurs along the trace of the focus. This makes it possible to produce any computer-generated structure in 3D (Fig. 5a), and the time taken to generate these structures is correlated with their complexity. For example, the structure shown in Figure 5a was written in about 5 min, since only the outer shell was polymerized by 2PP. After the polymerization process is completed, the non-irradiated resin can be developed out of the structure analogous to the processing of conventional 2D and 2.5D ORMOCER\(^\text{R}\) I structures and devices.\(^{[3]}\)

Due to the very sharp threshold fluence for the 2PP process, structure resolutions far beyond the diffraction limit can be realized. This is enabled by choosing a suitable combination of the pulse energy and the number of applied pulses. Since the optical losses of the ORMOCER\(^\text{R}\) I system are less than 0.2 dB/cm (at 1310 nm) and 0.55 dB/cm (at 1550 nm), the use of 2PP would be advantageous for the generation of integrated optical devices for telecom and datacom applications. Figure 5b shows an example of a photonic 3D crystal structure, which was generated in ORMOCER\(^\text{R}\) I on a glass substrate generated with 2PP. The production process took about 1 min. The periodicity of the crystal structure is about 450 nm, while the individual rod is approximately 220 nm in diameter.

It has to be mentioned, however, that the refractive index of the ORMOCER\(^\text{R}\) I resin \((n = 1.5382 \pm 0.0005\) at 633 nm) is still too low for a complete 3D photonic bandgap. Presently, the material is only suited for application in 1D photonic bandgap structures such as Bragg structures. Further material development will be carried out to increase the refractive index without loosing other advantages of ORMOCER\(^\text{R}\) such as low optical losses in the NIR, process flexibility, and good adhesion to various substrates.

4. Conclusions

An inorganic–organic hybrid polymer system has been described, which was synthesized by a modified sol-gel process. For waveguide applications, the refractive index can be adjusted by mixing with another inorganic–organic hybrid polymer. The optical loss of the material at data and telecom wavelengths (810, 1310, and 1550 nm) as well as at 780 nm is very low. The material can be processed by either conventional UV lithography or 2PP processes, where any arbitrary structure can be generated. Application examples for 2D, 2.5D, and 3D structures were given.

Further work on the material will be carried out in order to increase the refractive index.

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