Bottom-Up meets Top-Down – A Novel Approach towards 3-D Optical Devices

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ABSTRACT

Building materials from the bottom-up is complementary to conventional top-down materials processing. Inorganic-organic hybrid polymers designed for optical applications, were synthesized by hydrolysis/ polycondensation reactions, resulting in storage-stable resins built-up by nm-size organically functionalized primary particles (oligomers). The organically functional groups are typically oligo-(meth)acryl or styryl which allows one to pattern the resin by two-photon polymerization (2PP) processes using femtosecond lasers. With this method, any arbitrary structure can be directly written in three dimensions into the hybrid polymer with a resolution down to approx. 100 nm. The materials and the patterning process will be discussed with respect to applications in photonic devices.

Keywords: inorganic-organic hybrid polymers, two-photon polymeriaztion, photonic structures

1 Introduction

During the last decade, inorganic-organic hybrid polymers (ORMOCER®s) have attracted considerable attention for optical (microoptics, waveguides) or microelectronical (dielectrics, passivation) applications [1-3]. The properties of these multifunctional materials can be tuned towards the respective application which thus makes them promising also for photonics. The processing of ORMOCER®s consists of two steps: first, an inorganic-organic storage-stable sol is established by hydrolysis/polycondensation (sol-gel) reactions, followed by an organic cross-linking of the polycondensed alkoxysilanes due to their organic functionalities (e.g., methacryl or styryl moieties). The latter allows one to pattern the material by conventional photolithography [4] as well as using femtosecond laser pulses [5]. Both methods result in polymerized (solid) structures where the non-polymerized parts are removed by standard developers, whereas arbitrary 3-D structures can be written with the latter method.

2 Inorganic-organic hybrid polymers

Figure 1 shows a schematic sketch of the multifunctional precursors for the hybrid polymer synthesis as well as a brief overview about the variation of material properties. Generally, first an Si-O-Si network is established via polycondensation reactions of alkoxysilanes which yields organically modified nanoscaled inorganic-oxidic units.

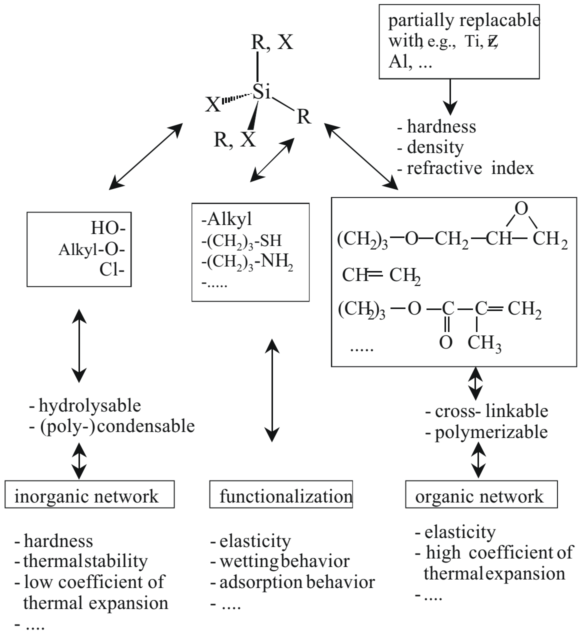

Figure 1: Schematic sketch of multifunctional precursors for hybrid polymers and the variation of properties.

The size of these inorganic units (typically 1 to 5 nm) is dependent on the alkoxysilanes and the reaction conditions (catalyst, concentration, solvent, temperature). Bi-substituted silanes yield chain or ring polymers, while tri-substituted silanes might result in three-dimensional networks. The Young modulus as well as the mechanical and thermal stability can be increased by increasing the amount of inorganics in the network. In addition, the coefficient of thermal expansion (CTE) and the optical losses in the near-infrared (NIR) regime are reduced as well.

A modification of the individual units influences the Young modulus and simultaneously the CTE of the

ORMOCER®s. In order to achieve highest transparency in the NIR regime, the material can be partially fluorinated or specific groups are replaced by perfluoroaryl groups, respectively. The organic polymerizable units are chosen depending on the requirements of the application. If UV lithography is applied for patterning, e.g., methacryl or styryl functionalities are chosen. Moieties such as alkyl or aryl groups connected to the Si also influence the material properties. It is likely that an increase in their amount within the hybrid polymer will reduce the degree of polymerization due to sterical reasons, thus resulting in a reduced density within the coated layers. In addition, these groups influence also the refractive index and the dielectrical properties.

Upon sol-gel processing, solvents are usually present in the resin. Typically, these are removed from the material in order to achieve highest processing flexibility. For thin-film applications, other solvents can be added to adjust the viscosity of the material. The resins storage stability without initiators at room temperature is about one year; for longer storage the resins should be cooled down (- 18 °C).

2 Two-photon polymerization

In this section, two-photon polymerization technique allowing the fabrication of arbitrarily complicated 3D nanostructures is described. It has recently been demonstrated by several groups [5-9] that two-photon-polymerization (2PP) of photosensitive materials allows the fabrication of three-dimensional microstructures. When tightly focussed into the volume of a liquid resin (which is transparent in the infrared), femtosecond laser pulses can initiate two-photon polymerization and produce structures with a resolution better than 0.1 µm. Compared to conventional photo-lithography which is a planar process, 2PP is a real three-dimensional volume micro- and nano-fabrication technique.

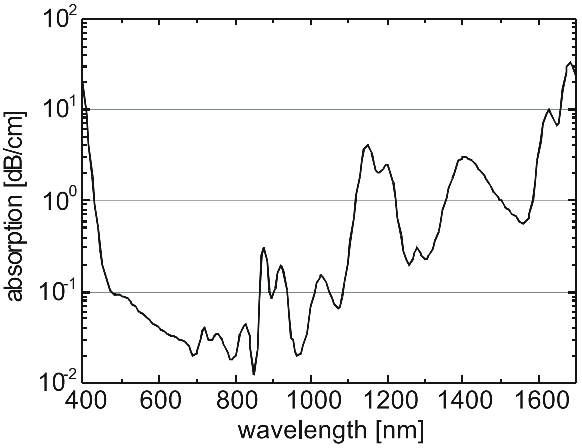

Figure 2: Absorption spectrum of an inorganic-organic hybrid polymer (ORMOCER®I) resin.

There is a strong demand for cheap and reliable materials such as, for example hybrid polymers, which can be photochemically patterned in two and three dimensions. Important advantages of these materials are: adjustable refractive index (in the range of 1.46 to 1.6), high optical transparency (Fig. 2) with low losses at data and telecommunication wavelengths (<0.06 dB/cm at 830 nm, <0.2 dB/cm at 1310 nm, and <0.6 dB/cm at 1550 nm), good thermal and mechanical properties, high chemical resistance, and quite low cost. These properties allow one to use ORMOCER®s for fabrication and rapid prototyping of different photonic structures and integrated optical devices.

These hybrid polymers are designed for ultraviolet (UV) lithography and contain initiators (e.g., Irgacure 369) sensitive to UV radiation with a single-photon absorption maximum at about 330 nm wavelength. In the near infrared, especially at 780 nm, these materials are transparent (Fig. 2) which allows one to focus femtosecond Ti:Sapphire laser pulses into the volume of the liquid resin. The experimental setup for real 3-D lithography is shown in Fig. 3.

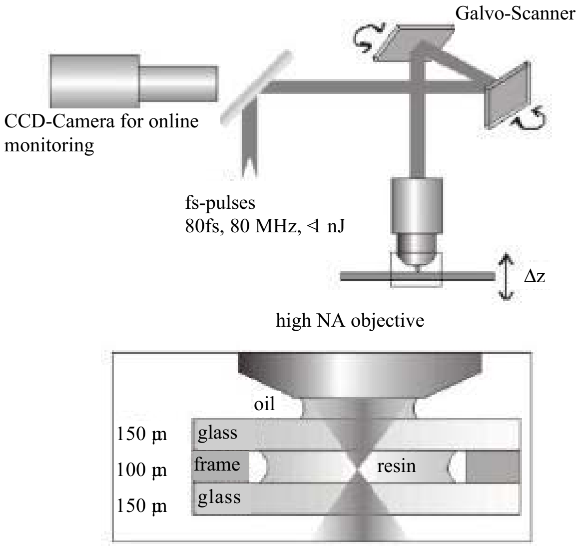

Figure 3: Experimental setup for 3D nanostructuring by means of 2PP.

The number of laser pulses and the irradiation time are controlled by an acousto-optical shutter with a minimum switching time of a few nanoseconds. Femtosecond laser pulses are focussed by a 100x immersion lens microscope objective having a numerical aperture of NA=1.4 and filled with a refractive index-matching oil (n_{oil}=1.515).

The high photon density in the focal volume triggers two-photon absorption by initiator molecules and results in the generation of radicals which, in turn, initiate the polymerization of the resin. All these processes are confined to a highly localized area at the focal point due to the quadratic dependence of the rate of radical formation on the laser intensity

$$\frac{\partial \rho}{\partial t} = (\rho_0 - \rho)\sigma_2 N^2 \quad , \qquad (1)$$

where σ_2 is the effective two-photon cross-section for the generation of radicals, N(r,z,t) is the photon flux, ρ_0 is the radical density at total conversion of initiator into radicals and ρ (r,z,t) is the density of radicals [5].

When the laser focus is moved through the resin in three dimensions, the polymerization occurs along the trace of the focus, i.e., any computer-generated 3-D structure can be fabricated by direct laser “writing” inside the volume of the hybrid polymer. The non-irradiated liquid resin can be, analogously to planar processing dissolved in a solvent (e.g., acetone), leaving the polymerized copy of the computer model.

In order to realize real 3-D microstructuring with femtosecond lasers, the laser beam was scanned with an x-y galvo-scanner and the sample was moved in the z direction with a translational stage. As a computer model, a Venus statue as shown in Fig. 4 (a) was used. To fabricate a 3-D microcopy of this statue, the laser beam is scanned in the horizontal plane along the contours shown in the central figure of Fig. 4. On the right side [Fig. 4 (c)], a scanning-electron microscope (SEM) image of a μ-scale Venus statue fabricated by 2PP is shown. In order to speed up the fabrication process which took approximately 5 minutes, only the outer shell was irradiated with femtosecond laser pulses. After that, the liquid resin was washed out and the statue was subsequently irradiated with UV light for final polymerization of the inner body.

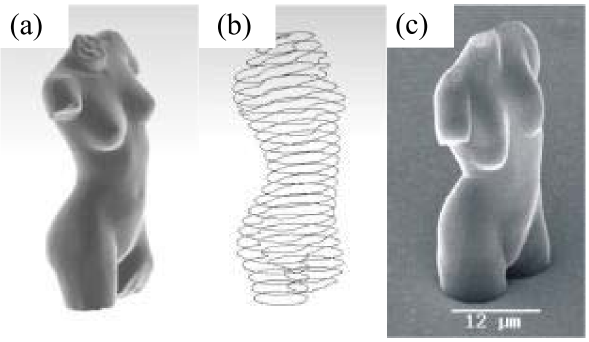

Figure 4: (a) Venus model used for the fabrication of 3-D micro-statue, (b) trace of the laser focus, and (c) SEM image of a μ-scale Venus fabricated by 2PP in ORMOCER®I.

Because of the threshold behavior and nonlinear nature of the 2PP process, a resolution beyond the diffraction limit can be realized by control of the laser pulse energy and the number of applied pulses. This is demonstrated in Fig. 5, where the measured data for the polymerized voxel (volume pixel) diameter are shown for different laser powers and irradiation times [5].

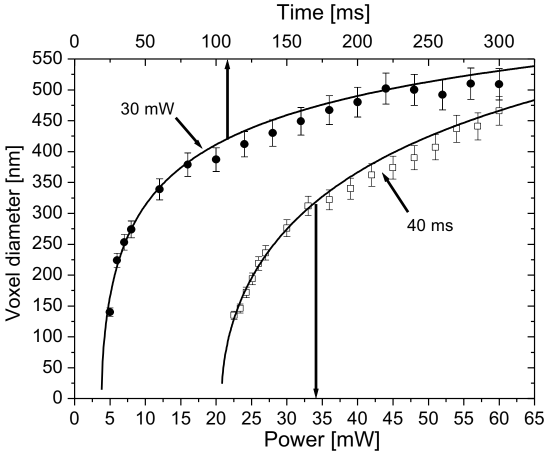

Figure 5. Measured data for diameter of the polymerized volume (voxel) as a function of the average laser power (for constant irradiation time $t = 40$ ms) and as function of the irradiation time (for constant laser power $P = 30$ mW).

Since the optical losses of ORMOCER®s are lower than 0.5 dB/cm at data and telecommunication wavelengths [1], the 2PP microstructuring technique is very attractive for the fabrication of micro-optical components and devices. In Fig. 6, an example of a ‘photonic crystal’ structure fabricated by 2PP in an ORMOCER® is shown. The structure was build up from individual rods with a diameter of about 200 nm and a spacing of 450 nm, respectively. The total fabrication time was 4 minutes.

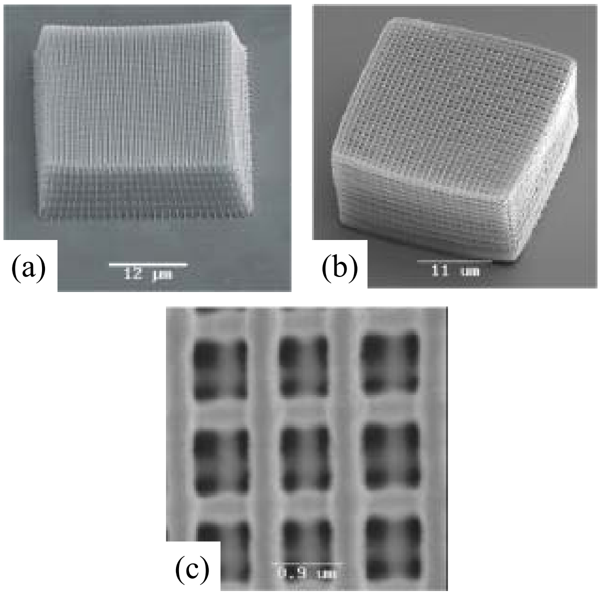

Figure 6: SEM images of ‘photonic crystal structures’ fabricated by 2PP in ORMOCER®I.

A major problem one always has to cope with when working with photosensitive resins in general is that the material shrinks upon cross-linking. For the 2PP process, shrinkage does not affect the 3-D geometry since each voxel shrinks to the same extent and remains exactly at the position of the controlled laser focus. During the final UV exposure process, however, further cross-linking takes place, leading to a pronounced shrinkage [c.f., Fig. 6 (a)]. This manifests itself in a distortion of the final 3-D structure compared to the computer model. This is due to a very good adhesion of the material to the substrate which can be seen as 'boundary condition', whereas this boundary condition is less present above the interface glass/ORMOCER®. Thus, the material can easily shrink upon cross-linking and distort the model, while at the interface the material is strongly bound to the substrates surface.

The more laser power is used, i.e. the higher the amount of polymerized units after laser irradiation, the less shrinkage occurs during the UV irradiation. Different pre- and post-treatments such as annealing the sample up to 80 °C have been tested in order to suppress the shrinkage which was not successful. For a compensation of the distortion caused by the shrinkage, the original model structure which is used to control the laser scanner was adapted such that the final structure shows no distortion after UV irradiation (Fig. 6 a and b). In Fig. 6 (c), a zoom into the structure depicted in Fig. 6 (b) is given which clearly shows the woodpile structure of the model.

Compared to other polymer materials, ORMOCER®s do not exhibit parasitic polymerization due to their microstructure (inorganic backbone), and the surface quality (particularly the rms roughness) is much better than for commercial acrylate systems [9]. It has to be mentioned, however, that the refractive index of the material has to be tuned towards higher refractive indices in order to account for a 3-D photonic bandgap. This is currently under investigation.

3 Conclusions

Inorganic-organic hybrid polymers and real 3-D patterning by two-photon absorption using femtosecond lasers seem to complement one another perfectly. The use of a bottom-up material with a top-down method promise not only to be a low-cost alternative for fabrication of components for applications in optics, medicine, and biology, but also opens a wide range for producing arbitrary three-dimensional micro- and nanostructures for the development of novel devices. By tuning the materials refractive index and by choosing a more suitable initiator with a high two-photon absorption cross-section, the fast fabrication of 3-D photonic crystal structures at any place on an optical chip will be feasible at fairly low cost.

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