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Optical polymers with tunable refractive index for nanoimprint technologies

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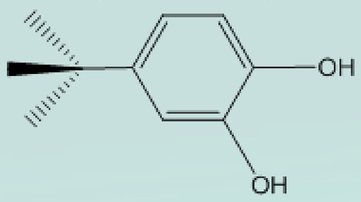
Introduction

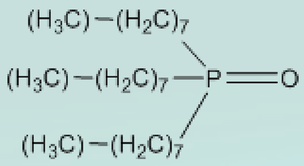
The fabrication of micro-optical elements is a key enabling technology for many applications and products of today. Here, we present our work on a functional imprint resist with a tunable refractive index for the fabrication of micro-optical elements with large area imprint technologies. Basic concept of the functional resist is the manipulation of the refractive index of the resist by the incorporation of TiO_2 nanoparticles in a polymeric matrix material (UV curable epoxy polymer). This work presents three different functional resist systems, each with differently in-situ stabilized TiO_2 nanoparticles having less than 10nm diameter, and compares these three materials. The refractive index of these three composite resist materials is manipulated e.g. at 635nm wavelength between 1.54 and 1.63 by adding up to 23wt% TiO_2 nanoparticles. Additionally the composite resist systems are highly transparent, also after temperature treatment, and they do not exhibit any significant shrinkage upon UV curing. Being usable for UV-enhanced Substrate Conformal Imprint Lithography (UV-SCIL), the composite resist systems fit for a cost-effective manufacturing of micro-optical elements.

TiO_2 nanoparticle synthesis

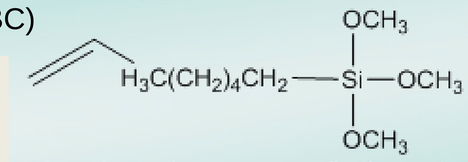
- The synthesis reaction for the TiO_2 nanoparticles is a non-aqueous alcoholic condensation [1]: $TiCl_4$ + benzyl alcohol with dissolved surfactants → TiO_2 + benzyl chloride.
- The particles were stabilized with three different surfactants (see Fig. 1) and dissolved in Tetrahydrofuran (THF) (see Fig. 2).
- Dynamic light scattering showed for all three surfactants a hydrodynamic radius of the particles below 10nm.



4-tert.-Butylcatechol (TBC)



Trioctylphosphineoxide (TOPO)



Trimethoxy(7-octen-1-yl)silane (TMOS)

Fig. 1: Molecular structure of the three surfactants

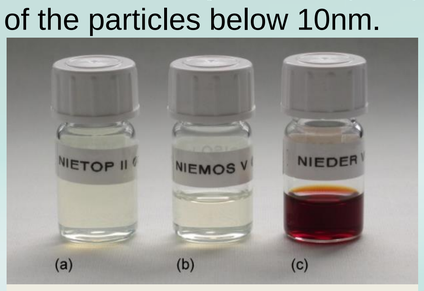


Fig. 2: Dissolved particles in THF: (a) TOPO stabilized, (b)TMOS stabilized and (c) TBC stabilized

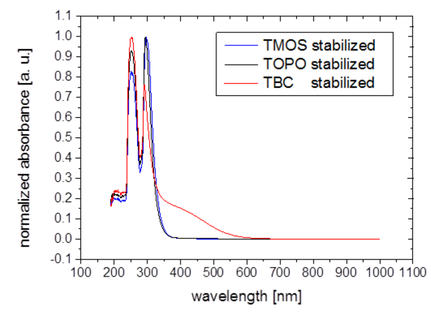


Fig. 3: UV/Vis measurement of the particle solutions

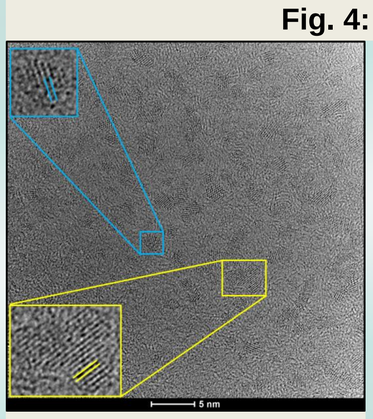
→ TBC stabilized particles absorb light in the visible spectrum from 350nm to 600nm (red color).

→ TOPO and TMOS stabilized particles are transparent for the visible light.

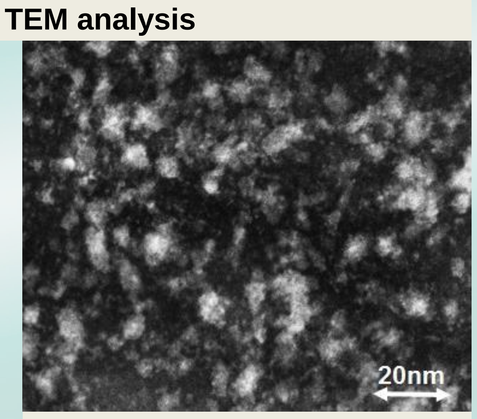
Functional optical imprint resist

- The UV curable organic imprint resist DELO-KATIOBOND OM VE 110707 [2] is dissolved in the THF particle solutions.
- After evaporation of the THF, the functional resist is prepared.

Fig. 4: TEM analysis



a) HRTEM image of functional resist layer with TOPO stabilized TiO_2 nanoparticles

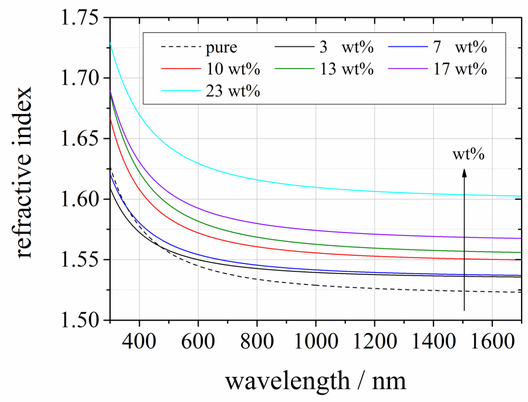


b) STEM image of functional resist layer with TMOS stabilized TiO_2 nanoparticles (bright spots).

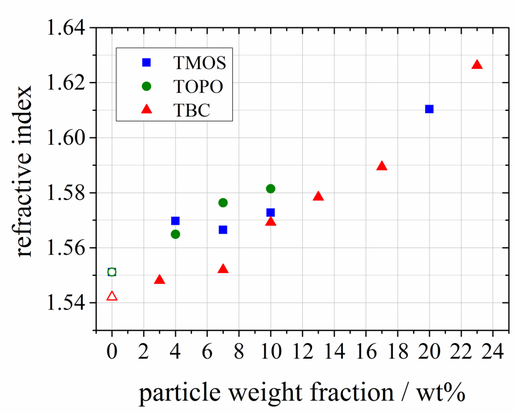
→ Crystalline and mono dispersed TiO_2 nanoparticles are homogeneously distributed in the polymer matrix.

→ The diameter for all three differently stabilized nanoparticles is below 10nm.

Fig. 5: Spectroscopic ellipsometry measurements



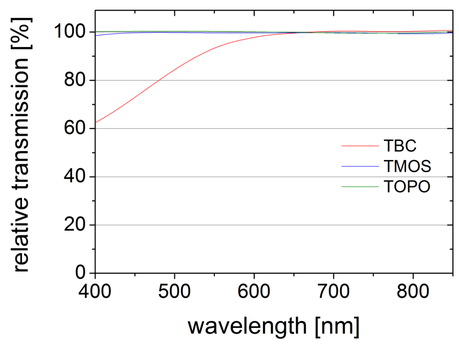
a) Wavelength dependent measurements of the refractive index of the functional resist with different wt% of TBC stabilized TiO_2 nanoparticles



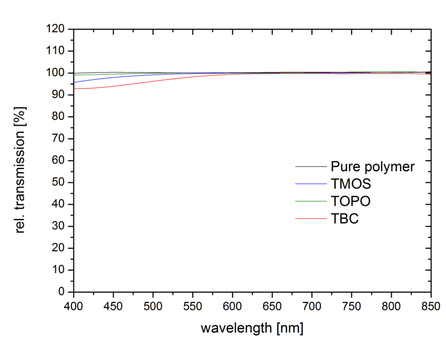
b) Refractive index of functional resists containing differently stabilized TiO_2 nanoparticles (TMOS, TOPO and TBC) at 633nm wavelength.

→ By adding TiO_2 nanoparticles the refractive index of the functional resist can be increased. The surfactant has no significant influence on the increase of the refractive index of the resist.

Fig. 6: Transmission and temperature stability



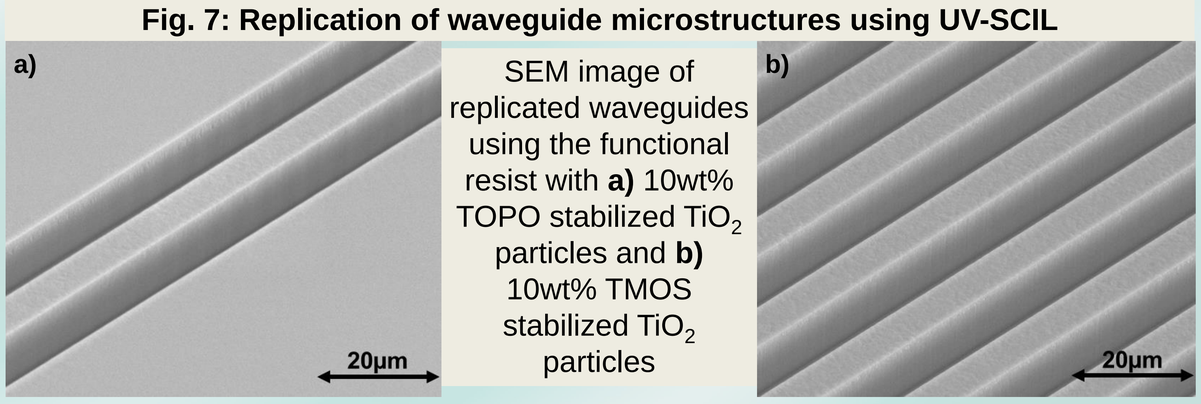
a) Relative transmission of functional resist layers in reference to the transmission of the pure matrix polymer



b) Relative transmission of the functional resist layers after 50s heat exposure at 220°C in reference to identical layers before heat exposure

→ The TiO_2 particles stabilized with TOPO have no influence on the transmission of the resist in the visible light spectrum, also after 220°C heat exposure.

Fig. 7: Replication of waveguide microstructures using UV-SCIL



SEM image of replicated waveguides using the functional resist with **a)** 10wt% TOPO stabilized TiO_2 particles and **b)** 10wt% TMOS stabilized TiO_2 particles

→ Functional resists with TBC, TMOS and TOPO stabilized TiO_2 particles can be used for the replication of micro optical structures with UV-SCIL
→ The ability of replicating nanostructures with UV-SCIL and similar functional resists was shown in a previous work of Fader et al. [3].

Conclusions

In conclusion, this work presents the comparison of functional optical resists for the direct fabrication of micro optical elements with UV-SCIL containing differently stabilized TiO_2 nanoparticles :

- By adding TiO_2 nanoparticles the refractive index of the functional resist can be increased. The surfactant has no significant influence on the increase of the resist's refractive index.
- With all three surfactants, crystalline and mono dispersed TiO_2 nanoparticles are homogeneously distributed in the polymer matrix with a particle radius below 10nm.
- The TiO_2 particles stabilized with TOPO have no influence on the transmission of the resist in the visible light spectrum, also after 220°C heat exposure.
- Functional resists with TBC, TMOS and TOPO stabilized TiO_2 particles can be used for the replication of micro optical structures and nanostructures with UV-SCIL.

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[1] M. Niederberger, G. Garnweitner, F. Krumeich, R. Nesper, H. Cölfen, M. Antonietti, Chem. Mater. **16**, 1202 (2004).
[2] R. Fader, H. Schmitt, M. Rommel, A.J. Bauer, L. Frey, R. Ji, M. Hornung, M. Brehm, and M. Vogler, Microelectron. Eng. **98**, 238 (2012).
[3] R. Fader, J. Landwehr, M. Rumler, M. Rommel, A.J. Bauer, L. Frey, R. Völkel, M. Brehm, and A. Kraft, Microelectron. Eng. **110**, 90 (2013).