Development of planarized digital transmission holograms on glass by embossing of thixotropic nano composites.

M. MENNIG, P. W. OLIVEIRA AND H. K. SCHMIDT

Institute for New Materials, gem. GmbH, Saarbrücken, Germany

1. Introduction

Holographic optical micropatterns on glass can be used for interesting applications like light guiding for architectural glazings, decorative purposes, product identification or holographic mirrors for projection screens in windows or for Head-up-displays in automotive and aircraft applications. The benefit of digital holographic micropatterns is their machine readability and brilliant optical performance. The planarization of embossed surface relief holograms by using an overcoat with different refractive index is important for improving the abrasion resistance and the copy safety of the micropatterns. Holographic micropatterns (volume phase holograms) can of course also be generated by laser interference methods using dichromate gelatine [1], which, however, is not durable enough for several applications.

There are basically two different techniques for embossing optical micropatterns in coatings on glass and other substrates: hot embossing [2-8] and reactive embossing [9-16]. For the hot embossing process, a heated stamper is pressed into a thermoplastic material and is removed after cooling. For the heating and cooling cycles process times between 25-60 min and processing temperatures of 100 °C to 180 °C are needed [17], which limits the production speed for obtaining a high optical quality of the micropatterns.

The reactive embossing process is based on curing of monomers, which have a very low and Newtonian viscosity. Therefore, the curing step must be carried out underneath the embossing stamper leading to a rather slow production speed.

A new class of non Newtonian material for high embossing speed processes on plastic foils has been developed recently [18]. This thixotropic nano composite material is based on an organic-inorganic matrix filled with ZrO_2 nano particles. The embossing process is performed after coating and drying. Due to the thixotropic character of the coating, its viscosity is decreasing, when the stamper is pressed in and it is rapidly increasing when the stamper is removed, so that the pattern can be fixed by a subsequent UV-curing step, so that the embossing step is separated from the curing step, which allows high processing speeds. Micropatterns with a periodicity of 500 nm and a pitch of 400 nm (CD-ROM) have been prepared with a line speed of 30 m/min [19].

The aim of this paper was to develop a thixotropic embossing coating material with low refractive index for glass (use of a flexible stamper) and a suitable high refractive index cladding for planarization. In order to understand the mechanism of generating thixotropy and in order to find a way to control the thixotopy, the effect of the concentration and the zeta potential of the SiO_2 nano particles in the sol was studied in this paper.

2. Experimental

For the preparation of an SiO_2-nanoparticulate sol, [20] 20.48 g (0.098 mole) of tetraethyl orthosilicate (TEOS) were added to 50.85 g ethanol (part A). 1.75 g of an 1 molar ammonia-solution are diluted with 34.41 g of water (part B). Hydrolysis and precondensation were performed by adding part A to part B after under rigorous stirring within 1 hour. After storing the mixture for 24 h at 70 °C, nano particles with 5 nm of radius are produced in a sol with a solid content of 5.5 wt.-%. The coating matrix was synthesized by adding 27 g (1.5 mole) water 236.12 g (1 mole) of 3-glycidoxypropyl trimethoxy silane (GPTS). After heating under reflux for 24 hours the solvent (methanol) was removed by vacuum distillation. To induce a

zeta potential variation of the SiO_2 nano particles, sols with 24 mg, 48 mg, 192 mg and 216 mg of tetrahexyl ammoniumhydroxide (THAH, 40 % in water) were added in each case to 107.5 g SiO_2-sol under fast stirring for 30 minutes at room temperature. 2.5 g of the GPTS-sol were added to the mixture and stirred for 30 minutes. After removing the solvent, the SiO_2-content is 70 wt.-%. A photoinitiator UVI 6974 (Union Carbide) was added in proportion of 1.2 wt.%. Finally the sol was filtered using a 0.4 µm filter.

The preparation of the TiO_2 nano particulate solution was performed as described in [21], using tetra isopropyl orthotitanate, isopropanol conc. HCl and water for the synthesis of TiO_2 nanoparticles under stirring at 25 ^{0}C for 24 h. For the surface modification of the TiO_2 nano particles, 2 g GPTS were mixed with 200 g TiO_2-sol under reflux with vigorous stirring at 50 ^{0}C for 5 hours. A part of isopropanol (10g) was removed from the sol by vacuum distillation at 14 mbar and 25 °C and 14 g of 2-isopropoxyethanol were added. Finally, a mixture of GPTS, hydrolysed with 0.1 N HCl by stirring for 24 h at 25° C and 2 wt.% (in relation to GPTS) of the photoinitator UVI 6974 (Union Carbide) was added. By this way a total TiO_2 content of 90 wt.% (related to the cured coating material) was reached.

Float glass substrates (50 mm x 50 mm x 2 mm) were coated with a GPTS/SiO_2 (70 wt.% of SiO_2) by dipping under clean room conditions (class 10000, air 30 ± 5 % relative humidity) using withdrawal speeds varied between 0.5 to 10 mm / s. One side of the substrate was covered by a protective tape. Flexible stampers were prepared from a digital Ni master using a silicone rubber (sil gel, Wacker) by molding and drying at 50 °C for 5 minutes. After drying of the coated gel films for 20 minutes at 100 °C, embossing experiments were performed. The rubber stamper was placed on a cylinder of about 20 cm in diameter an 35 cm in length and deposited on top of the gel layer by rolling and simultanous delamination of the rubber stamper from the cylinder. Afterwards, the stamper was loaded by a weight yielding to a pressure of about 8 mN / mm^2. After 30 s, the stamper was removed and the embossed structure was cured by UV-irradiation with an intensity of 10 mW / cm^2. The diffraction efficiency was measured as described in [22]. The cured embossed structure was coated with the TiO_2 sol by dipping with a withdrawal speed of 3 mm/s. The TiO_2 film was cured using 50 mW/cm^2 UV-irradiation and subsequent heat treatment at 100 °C for 1 min.

The viscosity of the sols was measured using a rotation viscometer (Pysica; Rheolab MC 120). The zeta potential of the SiO_2 particles was measured using a Zetasizer ESA-Sample SSP-1, MATEC. The morphology of the micro patterned coatings was investigated by profilometry, light microscopy and high resolution scanning electron microscopy.(HR-SEM).

3. Results and Discussion

3.1. Effect of the SiO_2 nano particle concentration on the structural viscosity of the nano composite

In a first step, the viscosity of SiO_2 coating sols with different amounts of SiO_2 nanoparticles were investigated before the final solvent (ethanol, water) removal. Fig. 1 shows the viscosity measurement of the nano composite sols in dependence of the shear stress rate.

As expected, the viscosity of the nano composite sol is increasing with the concentration of SiO_2 nano particles. However, the coating sols do not show any thixotropic behaviour. It was assumed that this was due to the too high solvent content, which avoids efficient interactions between the nano particles. Therefore, the solvent was removed by vacuum distillation in the next step.

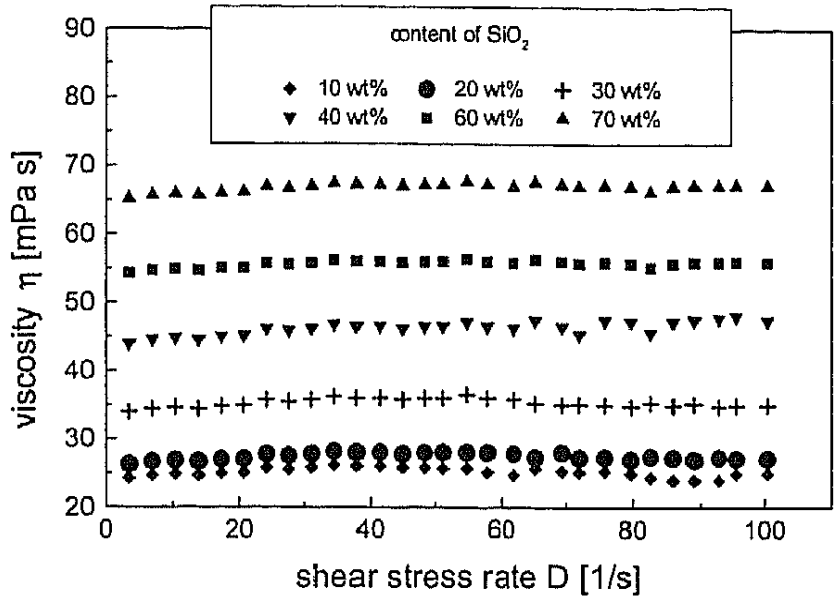


Fig. 1: Viscosity measurement of the GPTS/SiO_2 sol with 10 wt.%, 20 wt.%, 30 wt.%, 60 wt.% and 70 wt.% of SiO_2 (based on the amount of GPTS, without THAH) before removal of the solvent in dependence on the shear stress rate.

Fig. 2 shows the effect of the SiO_2 nano particles concentration on the GPTS matrix after the vacuum evaporation. It can be seen that the viscosity and the structural viscosity effect increases with the concentration of the SiO_2 nano particles.

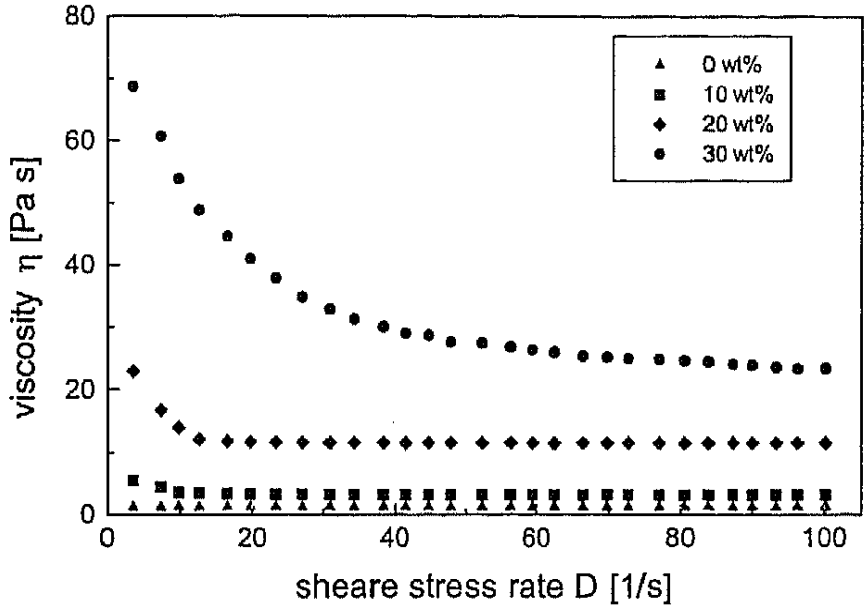


Fig. 2: Variation of the viscosity in dependence of the (increasing) shear stress rate of the GPTS/SiO_2 system with different concentrations of SiO_2 nano particles (0 wt.%, 10 wt.%, 20 wt.% and 30wt.%, without THAH).

The sols with an SiO_2 content of 20 wt% and 30 wt% clearly show structural viscosity. Appropriate measurements for sols with SiO_2 concentrations higher than 30% were not possible due the too high viscosity (the viscosity was out of the measurement range of the viscosimeter). It is also obvious from fig. 2, that the slope of the viscosity curve is much steeper for 20 wt% SiO_2 than for 30 wt%. This means, that the sol with a higher structural viscosity effect (with 30 wt.% of SiO_2) has a longer viscosity relaxation time, which could lead to a fast smoothening of the embossed structure in the time span after the removal of

the stamper and before UV curing. For the thixotropic embossing of digital micropatterns, a high structural viscosity effect and a short relaxation time is required. The relaxation time is dependent on the strength of the interparticulate forces, which can easily be controlled by the Zeta potential of the nano particles, which now was investigated in the next step.

3.2. Effect of the Zeta potential of the SiO_2 nano particles on the structural viscosity of the nano composite sols

The variation of the dynamical viscosity in dependence of the shear rate for GPTS/SiO_2 nano composite sols with different concentrations of THAH (24 mg, 48 mg, and 192 mg) is shown in Fig. 3.

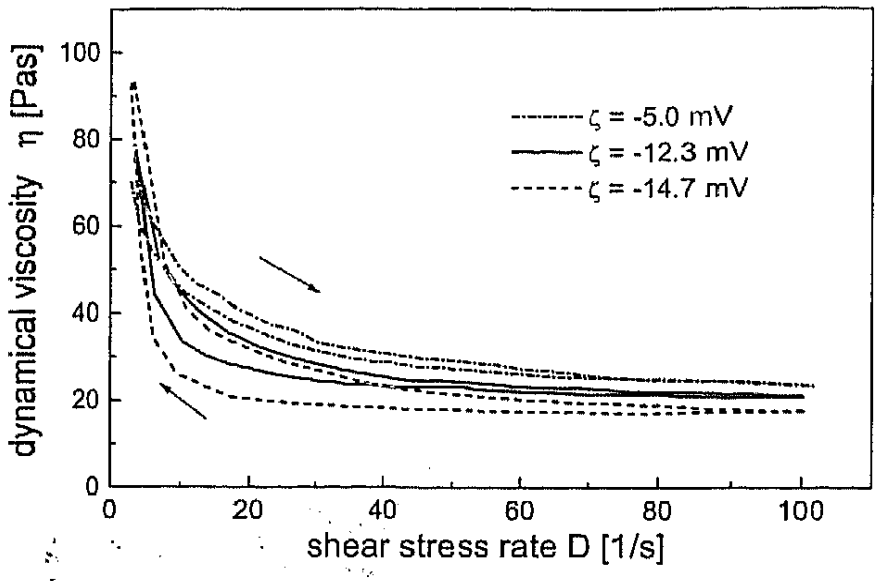


Fig. 3: Variation of dynamical viscosity in dependence of shear stress rate of GPTS/SiO_2 with 30 wt% of SiO_2 nano particles with different concentrations of THAH (24 mg → ζ = –5.0 mV, 48 mg → ζ = -12.3 mV and 192 → ζ = –14,7 mV).

The addition of 24 mg THAH to the GPTS/SiO_2 sol leads to a Zeta potential (ζ) of the SiO_2 of -5.0 mV, 48 mg to -12.3 mV and 192 mg to -14,7 mV. From Fig. 3 one can see, that the variation of the concentration of THAH has a strong influence on the rheological behaviour of the sols. The dynamic viscosity curve for ζ = -5 mV is still rather similar to the curve without THAH (see fig.2). The slopes of the curves become significantly steeper in the low shear rate range between D = 0 1/s to D = 30 1/s with increasing THAH content. This is especially obvious for the branches of decreasing shear rate, which is important for the embossing process. This means, that the relaxation time of the nano composite is shorter at higher concentration of THAH. This seems to be plausible, because the absolute value of the ζ-potential - and therefore the amount of electrical charge on the particles – is increasing with increasing THAH content. This leads to higher repulsive forces between the particles and therefore to shorter relaxation times.

3.3. Embossing experiments

For the embossing experiments, coatings with 60 wt% of SiO2, modified with THAH were used. Their viscosity was low enough to allow the use of a flexible silicone rubber stamper, prepared as a true copy of a Ni-shim with a digital pattern of 0.3 – 1 µmin depth. This is advantageous, when large areas (here 50 x 50 mm^2) have to be embossed on glass substrates. The curing time delay (time interval between removing of the stamper and UV irradiation) was varied and the quality of the embossed hologram was evaluated by a diffraction efficiency measurement [22]. The result is presented in fig. 4:

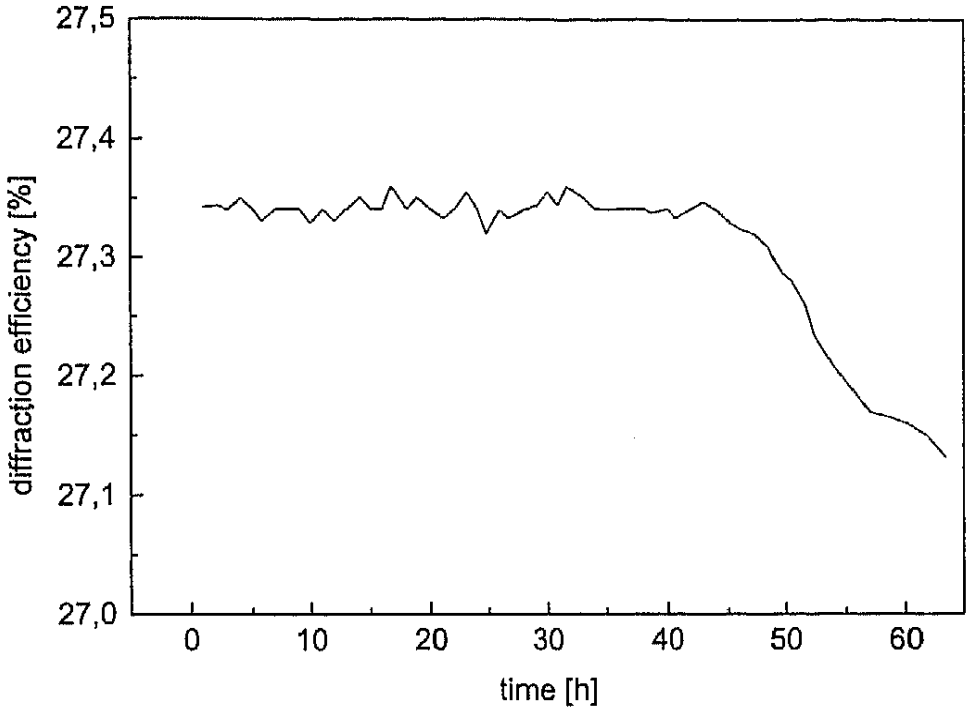
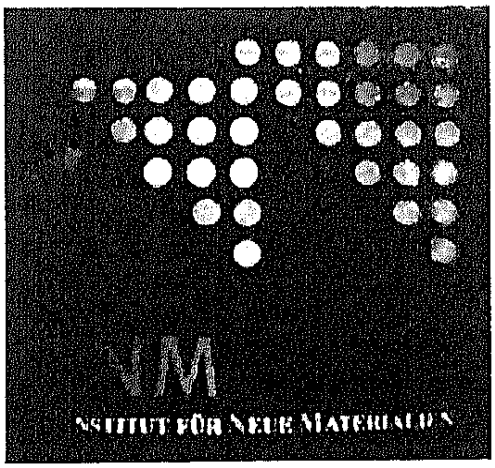


Fig. 4: Diffraction efficiency measurement at λ = 633 nm in dependence of time of a reference uncured area of the hologram.

The diffraction efficiency measurement is a very useful and sensitive method to detect small changes in the holograms or µm structures. The diffraction efficiency was measured in the coloured spots of the INM-logo (see fig. 5). Fig. 4 shows that a diffraction efficiency of about 27 % was obtained. This is a little bit lower than the theoretical maximum value of 34 %. The reason for this difference may be due to a not optimised depth of the replica or the stamper and will have to be investigated in the future. Fig. 4 also shows, that the diffraction efficiency starts to decrease only after 45 h. This curing time delay is by far long enough for embossing applications. Systems with lower contents of SiO_2 nano particles have not been investigated yet. Fig. 5 shows the picture of the embossed transmission hologram.

a)



b

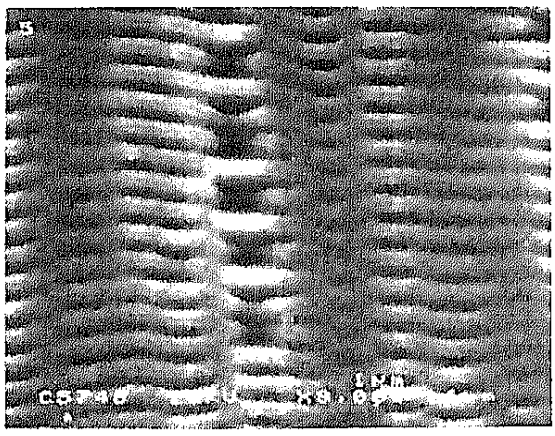


Fig. 5:a) photo of the UV cured embossed hologram, b) micrograph inside of one of the bright spots in fig. 5 a)

The optical appearance is very brilliant under suitable illumination in a narrow angle of view. The hologram is almost invisible (e.g. clear and colourless) outside this range. This means that the nanoparticles must be very well dispersed, because there is no scattering, despite the high content of nano particles. As one can see from fig 5 b), a sharp edged, crack free micropattern could be obtained. The shrinkage of the embossing material can be roughly estimated to be below 2 %, due to high amount of nano sized SiO_2 filler particles.

After coating the hologram with the TiO_2 layer, no surface relief could be detected by HR SEM anymore. The coating was crack-free and showed good adhesion to the micropatterned layer. The diffraction efficiency at 633 nm wavelength dropped slightly from 27 % (after curing) to 24% after the deposition with TiO_2 film and final curing. The diffraction efficiency of the hologram is dependent on the refractive index difference (Δn) between the structured material and the neighbourhood. The Δn between the GPTS/SiO_2 embossing material and air is 0.47 and between GPTS/SiO_2 and TiO_2 coating is 0.43, which can explain the small decrease of the diffraction efficiency.

4. Conclusion

Soft, thixotropic nano composite gel films have been developed, which are suitable for the preparation of digital optical micropatterns on glass by embossing with flexible stampers and appropriate low embossing pressures. The thixotropic character of the embossing material can be controlled by the amount of SiO_2 nanoparticles and especially by tailoring their ζ-potential, which is the more important tool to tailor the rheology, because it affects the interparticulate forces. The ζ-potential can be easily controlled by modification of the particle surface with charged molecules. Simultaneously, this avoids agglomeration and allows therefore the preparation of composites with high SiO_2 particle content and excellent optical quality. Low shrinkage and a low refractive index are welcome side-effects of this high SiO_2 content.

The copy safety of the holograms could be improved significantly by filling the surface relief with a high index TiO_2 based nano composite without deteriorateting the high brilliance of the holograms. This planarization is also an important prerequisite for a high durability and abrasion resistance, which will be investigated in the near future.

5.Acknowledgements

The authors thank Dr. A Gier for the preparation of the stamper, Mr. U. Dreier for the sol preparation and Dr. M. Jilavi for the HR-SEM investigations. The authors also thank the Federal Ministry of Research and Technology and the State of Saarland for the financial support.

6. References

[1] T. A. Shankoff, Phase holograms in dichromated gelatin, Appl. Opt. **7**, (1968) p. 2101-2105,

[2] C. Puech, Optics communication, Vol. **7**, Nr. 2, Februar 1973, S. 135-138

[3] G. D. Aumiller, E. A. Chandross, W.J. Tomlinson, H.P. Weber, J. of Applied Physics, Vol. **45**, Nr. 10, Oktober 1974, S. 4557-4562

[4] R. Ulrich, H.P. Weber, E. A. Chandross, W.J. Tomlinson, E.A. Franke, Applied Physics Letters, Vol. **20**, Nr. 6, März 1972, S. 213-215

[5] R. Waldhäusel, P. Dannberg, E. B. Kley, A. Bräuer, W. Karthe, International Journal of optoelectronics, Vol. **8**, Nr. 5/6, 1993, S. 529-536

[6] P. Dannberg, E. B. Kley, Th. Knoche, A. Neyer, in Integrated optics and microoptics in polymers, ed. Wolfgang Ehrfeld, Leipzig, Teubner, 1993, S. 211-218

[7] A. Picard, W. Ehrfeld, H. Löwe, H. Müller, J. Schulze, SPIE's 42nd Anual Meeting International Symposium on Optical Science, Engineering and Instrumentation, 1997
[8] L. Baraldi, R.E. Kunz, J. Meissner, SPIE Vol. **1992** Miniature and Micro-Optics and Micromechanics, 1993, S. 21-29
[9] M. Tanigami, S. Ogata, S. Aoyama, T. Yamashita, K. Imanaka, IEEE Photonics Technology Letters, Vol.**1**, Nr. 11, 1989, S. 384-385
[10] F. P. Shvartsman, SPIE Vol. 1507 Holographic Optics III: Prinziples and Applications, 1991, S. 383-391
[11] T. E. Yeo, N.J. Phillips, S.J. Clements, S. Ojha, International conference on holographic systems, components and application London UK: IEE **4**,1993, S. 186-**191**
[12] K. Goto, K. Mori, Japanese, J. of Applied Physics, Vol. **31**, 1992, S 1586-1590
[13] N. Thoge, A. Matsuda, T. Minami; J. Non-Cryst. Sol. **128** (1988) 501
[14] W. Lukosz, K. Tiefenthaler; Opt. Lett. (1984) 537
[15] H. Schmidt, H. Krug, N. Merl; J. Non-Cryst. Sol. **147-48** (1992) 447
[16] A. Gombert et al; Thin Solid Films **351** (1999) 73-78
[17] Ruprecht, W. Bacher, V. Plotter, L. Schmidt, Abformen mit ungefüllten und gefüllten Kunststoffen, Forschungszentrum Karlsruhe, Wissenschaftliche Berichte, FZKA-5670, 1995
[18] A. Gier, N. Kunze, M. Mennig, P. W. Oliveira, S. Sepeur, B. Schäfer, H. Schmidt, DE 10001135 A1, 13.01.2000
[19] M. Mennig, A. Gier, P. W. Oliveira, H. Schmidt, Proceedings Annual Meeting of the Deutsche Glastechnische Gesellschaft, Halle, 1999
[20] A. Frantzen, Dissertation, University of Saarbrücken, 2002
[21] Oliveira, P.W., H. Krug, A. Franzen, M. Mennig, H. Schmidt, Sol Gel Optics IV, SPIE-The International Society for Optical Engineering (1997), 452-461
[22] Oliveira P.W., Krug H., Künstle H., Schmidt H.. „The production of Fresnel lens in Sol-Gel derived ormocers by Holography" SPIE- The international Society for Optical Engineering Vol **2288**, pp554-562 (1994)