2.4.1 EMBOSSING

M. Mennig, P. W. Oliveira, H. Schmidt

1. INTRODUCTION

Layers with surface relief patterns in the μm to 100 nm range are used for optical applications like holograms, gratings, micro lens arrays, light guiding elements (wave guides, diffusers, reflectors, converters for head-up displays) or optical data storage (CD-ROM) and also for electronic applications (resists for the semiconductor industry). Another large scale field of application is haptic, e. g. the surface of touch input panels.

Well established technologies for their realization are injection molding (CD-ROM fabrication), laser writing [1] (CD-ROM "burning"), lithography [2,3] using mask-aligner techniques [4] for optical waveguides and electronic application and also embossing [5,6].

Embossing is a process in which the negative surface relief of a stamper (planar or roll) is replicated by pressing the stamper into the material, the obtained patterns being fixed by curing or cooling and removing the stamper. The stampers are fabricated by expensive and time consuming techniques like holography, laser writing or mechanical stitching all with subsequent Ni deposition by electro plating or even by electron beam etching of glass surfaces for very fine (< 100 nm) patterns.

The costs for the embossed components become therefore reasonable by the manifold replication of this expensive master pattern. Another advantage, compared to lithography is that micropatterns with complicated cross sections can be obtained in a single step, whereas lithography would require several cycles of "coating, illumination and developing or etching". For the fabrication of arrays (like micro lens arrays) which consist of single elements that have to be adjusted to each other, the embossing technique offers the additional advantage that not only the elements themselves but also their alignment can be replicated in a low cost process.

With special respect to the sol-gel technique, two general cases of embossing are discussed in the next two sections: The first one is the embossing of organic-inorganic hybrid materials and nanocomposites, which is characterized by a low temperature processing. This kind of technology is strongly related to organic polymers (mostly acrylates). The general advantages of the sol-gel derived materials are:

- higher scratch hardness and better chemical durability
- lower shrinkage and therefore better near-net shaping
- lower thermal expansion and water up-take
- tailorable etch resistance (electronic applications)

The second case refers to glass-like micropatterns where the sol-gel technique offers unique possibilities for applications.

2. EMBOSSING OF ORGANIC POLYMERS AND ORGANIC-INORGANIC COMPOSITES

The fabrication of microstructures with organic polymers plays an important role for different industrial applications like holographic elements, gratings, micro lenses, etc. However these materials have a low thermal stability and a poor scratch hardness [7]. The combination of an organic and an inorganic network as produced by the sol-gel process opens the possibility of tailoring materials in a wide range with respect to their optical and mechanical properties and it provides a very attractive route for synthesizing and developing materials for optical applications [8]. There are basically three different embossing techniques for the fabrication of micropatterns: hot embossing [9-15], reactive embossing [16-19] and thixotropic embossing [20,21].

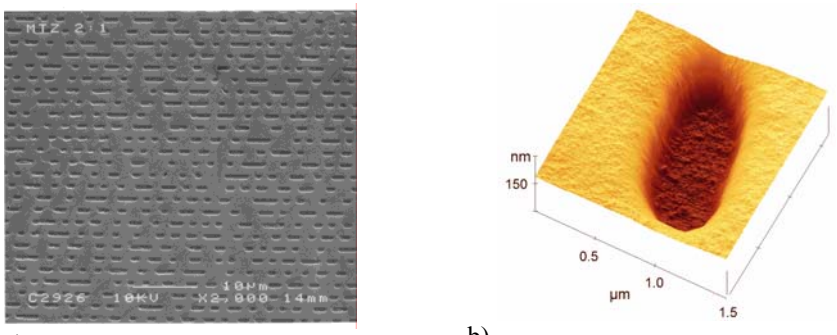
The *hot embossing* process is used for the micropatterning of thermoplastic materials. Usually, both the material and the stamper are heated up to temperatures well above the transition temperature of the material before the stamper is pressed onto it. Before removing the stamper, the patterned layer has to be cooled down in order to avoid a deformation of the surface relief by a viscous flow process. This limits the production speed [22], especially for the fabrication of binary (e. g. machine-readable) optical micropatterns. Shvartsman [17] and Chon [23] have shown that sub-μm patterns with edge inclinations of about 80° could be prepared by hot roller embossing with a maximum line speed of 10 m/min. Naturally, the hot embossing technique cannot be applied to large area substrates by stepping. This is disadvantageous especially for extra fine (< 100 nm) patterning in electronic industries on large areas (> 4" wafers).

In *reactive embossing*, the stamper or master roll is pressed onto a low viscous, liquid layer of organic monomers (mostly acrylates), uncured organic-inorganic hybrid materials [24] or organic-inorganic nanocomposites [25-27] respectively. In all cases the embossed micropattern has to be fixed by curing the material (mostly by UV-irradiation) underneath the stamper. This also limits the production speed, especially for patterns with steep walls and sharp edges. Another problem of this technique is the shrinkage during curing, which can limit the near-net shaping of the product. It has been shown that this can be overcome by using oxide nanoparticles as transparent fillers in organic-inorganic nanocomposites [25-27].

For the fabrication of patterns in the sub-mm and mm-range, which are used for instance for anti-slip shoes or floor coverings, *thixotropic embossing* tech-

nique is used [28,29]. In this case, the material to be embossed has to have a thixotropic behavior [30]. When the stamper or embossing roll is pressed onto it, a high shear stress is applied and the viscosity of the material decreases and the surface relief of the stamper is easily filled with the embossing material. When the stamper is moved out of the material, the shear load decreases and, consequently, the viscosity increases drastically. Due to this high viscosity, the surface relief of the embossed layer can be conserved for the short time span between the removing of the stamper and the final curing. It is obvious that the separation of these two steps allows high processing speeds. Thixotropic material's properties can be obtained by using thixotropic agents like hydroxy propyl cellulose or by adding sub-µm fine powders like Aerosil® (SiO_2 -particles). However, such composites are usually not transparent due to light scattering effects and therefore they are not suitable for optical micropatterns.

It has been shown recently [20,21] that the general approach of *thixotropic embossing* can also be applied for the preparation of digital optical micropatterns. In this case, the thixotropic character of the embossing material is realized by the incorporation of ZrO_2 nanoparticles in a UV curable, highly condensed organic-inorganic matrix. Due to the very small size (≈ 5 nm) of the ZrO_2 nanoparticles, light scattering can be neglected in first approximation. On the other hand, the small particle size leads to large internal interfaces in the composite materials, which can be used to tailor the rheology of the composite by appropriate surface modification of the particles. Such materials exhibit a strong thixotropic behavior and can be used to obtain transparent embossing coatings on plastic foils. The process has been demonstrated to produce CD-ROM-like patterns with a periodicity of 500 nm, a pitch of 400 nm and a depth of about 150 nm by a roller embossing process with a line speed of up to 30 m/min [27]. Figure 1 shows a SEM micrograph of this surface relief (1a) and an AFM picture of a single CD-ROM pitch (1b).



a) b)

Figure 1. a) SEM micrograph of a CD-ROM like surface relief prepared by roll embossing of a thixotropic nanocomposite layer on a plastic foil with a line speed of 30 m/min and subsequent UV-curing [20]. b) AFM picture of a single pitch from figure a.

As one can see from figure 1a, the upper surface of the embossed pattern is very smooth and all pitches are well defined and seem to have the same depth. Fig 1b proves that the walls of the pitches are very steep (89°). The roughness at the bottom of the pitch is however higher than that of the top surface, which is due to the quality of the used stamper.

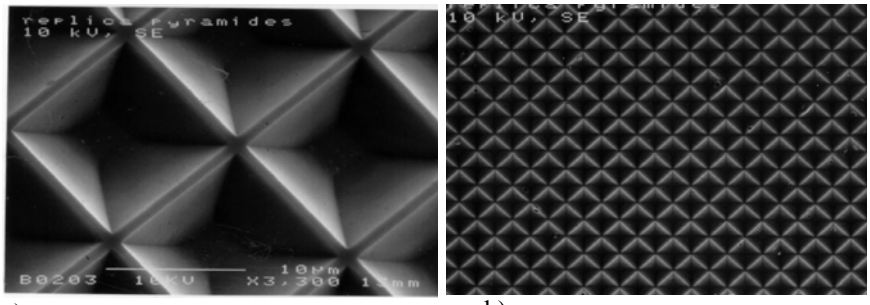
Furthermore it could be shown that this method is also suitable to prepare well defined digital micropatterns with structural depths of up to 350 nm on large area (18 x 30 cm^2) [20].

3. EMBOSSING OF GLASS-LIKE SOL-GEL COATINGS

The deposition of micropatterned glass-like layers on large area flat glass surfaces is very interesting for light-guiding or photovoltaic (light-trapping) [31] application. The latter requires sharp edged pyramidal patterns with dimensions (base line and height) of about 50 μm. The state-of-the art technology – the roll embossing of the hot glass preformed directly after the glass production – cannot be used in this case as it does not allow the generation of sharply edged micropatterns because of the low viscosity (high temperature) and slow cooling rate. The application of organic polymers or organic-inorganic embossing materials is not possible, with respect to the high temperature processing of the photovoltaic cells (550 °C) [31]. Furthermore, excellent chemical resistance and improved mechanical properties like scratch resistance are required.

Inorganic silica or silica titania films prepared from tetraethoxy orthosilicate and titanisopropylate were used to produce relief patterns with 1200 lines/mm and with heights up to 150 nm. These materials have exceptional mechanical strength and hardness, a high transmission between 170 and 3400 nm, a very low coefficient of thermal expansion and a high chemical and thermal durability. On the other side, the state-of-the-art of these glass-like materials used for micropatterning by embossing show two main disadvantages. The films shrink about 60-70 % after densification, so that a near net shaping is not possible. Furthermore, the thickness is limited to 80 up to 200 nm [32] and the embossing depth obtained by this technique is extremely small [33-37]. Another disadvantage of these materials is that rather high pressures of several bar are needed, which requires the use of rigid (metal) stampers. This is problematic for the patterning of large area flat glasses, which exhibit a waviness of about ± 5 μm on 1 m length scale.

In order to solve all these problems, soft gels based on methyl and phenyl modified alkoxysilanes and colloidal silica particles have been developed recently [31,38,39]. They allow the use of flexible stampers (prepared from silicone rubber) and a crackfree densification of patterns with structural heights of about 30 μm at 500 °C on glass as shown in figure 2.



a) b)

Figure 2. HR-SEM picture with (left picture with a 20° tilt) of an embossed pyramidal structure after densification at 500 °C [31].

As one can see from figure 2, sharp edged crackfree replica could be obtained. The structural height, determined by profilometer, was about 30 µm. The pattern appears clear and transparent and inclusion of carbon cannot be detected visually or by microscopy. Furthermore it is assumed that the ethanol vapor, generated during the gelation at 50 °C, can penetrate through the silicone rubber stamper more easily compared to Si or metal stampers.

The comparison of structural height of embossed samples before and after firing shows that the vertical shrinkage during firing is about 25 %, a value much lower than for micropatterns from TEOS gels (60 to 70 % [34]). The low shrinkage is due to the rather high SiO_2 content of the sol (296 g/l) and to the fact that the methyl and the phenyl groups are burned off at temperatures in the range between 550 °C to 600 °C [39].

Both effects can be attributed to the addition of the colloidal silica particles which act as a filler and also allow the formation of rather dense glass like materials (95 % density) as obtained from refractive index measurements [40] after firing at 500 °C.

4. REFERENCES

1. H. Schmidt, H. Krug, R. Kasemann, F. Tiefensee, Development of optical waveguides by sol-gel techniques for laser patterning, in: SPIE Proceedings "Submolecular Glass Chemistry and Physics", P. Bray, N. Kreidl, **1590**, 36 (1991)
2. L. d'Auria, J.P. Huignard, A.M. Roy, E. Spitz, Photolithographic fabrication of thin film lenses, Optics Communications, **5(4)**, 232 (1972)
3. T. Fujita, H. Nishihara, J. Koyasama, Blazed gratings and Fresnel lenses fabricated by electron-beam lithography, Optics letters, **7** (12), 113 (1982)
4. H. Krug, N. Merl, H. Schmidt, Micropatterning of organic-inorganic nanocomposites for micro-optical applications, J. Non Cryst. Solids, **147-148**, 447 (1992)
5. R. Ulrich, H.P. Weber, E.A. Chandross, W.J. Tomlinson, E.A. Franke, Embossed Optical Waveguide, Applied Physics Letters, **20 (6)**, 213 (1972)
6. H. Krug, B. Zeitz, P.W. Oliveira, H. Schmidt, Fabrication of microlens arrays from sol-gel composites by embossing techniques, in: Advanced Materials in Optics, electro - optics and communication technologies, P. Vincenzini, G.C. Righini (eds.), National Research Council, Italy, 501 (1994)

7. H. Schmidt, Die Rolle maßgeschneiderter Werkstoffe für zukünftige Technologien, VDI Berichte Nr. 1198, 59 (1995)
8. H. Schmidt, H. Krug, R. Kasemann, N. Merl, V. Gerhard, F. Tiefensee, S. Brück, in: Homage to Galileo, P. Mazzoldi (ed.) University of Padova, Italy, 303 (1992)
9. C. Puech, Thin film optical components duplication method, Optics communication, **7 (2)**, 135 (1973)
10. G. D. Aumiller, E. A. Chandross, W. J. Tomlinson, and H. P. Weber, Submicrometer resolution replication of relief patterns for integrated optics, J. Appl. Phys., **45**, 4557 (1974)
11. R. Ulrich, H.P. Weber, E. A. Chandross, W.J. Tomlinson, E.A. Franke, Embossed Optical Waveguides, Applied Physics Letters, **20 (6)**, 213 (1972)
12. R. Waldhäusl, P. Dannberg, E.B. Kley, A. Bräuer, W. Karthe, Highly efficient blazed grating coupler in planar polymer waveguides, Int. J. of Optoelectronics, **8 (5/6)**, 529 (1993)
13. P. Dannberg, E. B. Kley, Th. Knoche, A. Neyer, in: Integrated optics and microoptics in polymers, Wolfgang Ehrfeld (ed.), Leipzig, Teubner, 211 (1993)
14. A. Picard, W. Ehrfeld, H. Löwe, H. Müller, J. Schulze, SPIE's 42nd Annual Meeting International Symposium on Optical Science, Engineering and Instrumentation (1997)
15. L. Baraldi, R.E. Kunz, J. Meissner, High-precision molding of integrated optical structures, SPIE "Miniature and Micro-Optics and Micromechanics", volume **1992**, 21 (1993)
16. M. Tanigami, S. Ogata, S. Aoyama, T. Yamashita, K. Imanaka, Low-wavefront aberration and high-temperature stability molded micro Fresnel lens, IEEE Photonics Technology Letters, **1 (11)**, 384 (1989)
17. F. P. Shvartsman, Dry photopolymer embossing: novel photoreplication technology for surface relief holographic optical elements, SPIE, "Holographic Optics III: Principles and Applications", **1507**, 383 (1991)
18. T.E. Yeo, N.J. Phillips, S.J. Clements, S. Ojha, International conference on holographic systems, components and application London UK: IEE 4, 186 (1993)
19. K. Goto, K. Mori, Japanese, J. of Applied Physics, **31**, 1586 (1992)
20. M. Mennig, A. Gier, S. Schmidt, Large area holographic surface relief micropatterns by embossing of thixotropic nanocomposite layers on plastic substrates, Deutsche Glas Gesellschaft (1999)
21. M. Mennig, Verfahren zur Herstellung eines mikrostrukturierten Oberflächenreliefs durch Prägen thixotroper Schichten, Patent PCT/EP01/00333
22. Ruprecht, W. Bacher, V. Piotter, L. Schmidt, Abformen mit ungefüllten und gefüllten Kunststoffen, Forschungszentrum Karlsruhe, Wissenschaftliche Berichte, FZKA-5670 (1995)
23. S.Y. Chou L. Zhuang, X. Sun, Multilayer Resist Methods for Nanoimprint Lithography on Non-Flat Surfaces, J. Vac. Sci. Technolo. B., **16 (6)**, 3922 (1998)
24. A. Gombert, W. Glaubitt, K. Rose, J. Dreibholz, B. Bläri, A. Heinzel, D. Sporn, W. Döll, V. Wittwer, Periodic Surface-Relief Structures on Large Areas for Optical Applications, Thin Solid Films, **351 (1,2)**, 73 (1999)
25. H. Schmidt, H. Krug, N. Merl, Micropatterning of organic-inorganic nanocomposites for micro-optical applications, J. Non-Cryst. Sol., **147-148**, 447 (1992)
26. H. Schmidt, H. Krug, Inorganic-organic polymers for micro-optic applications, Fachbeitrag VTE, 468 (1992)
27. H. Krug, N. Merl, H. Schmidt, Micropatterning of organic-inorganic nanocomposites for micro-optical applications, Teubner-Texte Phys. 27 (Integrated Optics and Micro Optics with Polymers), 192 (1993)
28. M. Uryn, S. Odate, N. Takayama, K. Sei, Kanebo NSC, Finishing Elastic Pavement surfaces on athletic fields, JP 03096504 AZ, 22.04.1991
29. M. Nakanishi, Suzuki Sogyo KK, Embossed polyurethane rubber sheets for shoe soles, JP 06000826 AZ, 11.01.1991
30. H. Green, Industrial Rheology and Rheological Structures, John Wiley & Sons, Inc.: New York, U.S.A., 143 (1949)
31. M. Brendel, D. J. A. Werner, A. Gier, M. Mennig, H. Schmidt, Sol-Gel coatings for light trapping in crystalline thin films silicon solar cells, J. Non-Cryst. Sol., **218**, 391 (1997)
32. F. Lange, Proceedings of the international symposium on molecular level designing of ceramics, 14-28, Nagoya, Japan (1991)

33. R. L. Roncone, L. A. Weller-Brophy, L. Weisenbach, J. J. Zellinski, Embossed Gratings in Sol-Gel Wave-Guides - Pre-Emboss Heat- Treatment Effects, J. Non-Cryst. Sol., **128**, 111 (1991)
34. N. Tohge, A. Matsuda, T. Minami, Y. Matsuno, S. Katayama and Y. Ikeda, Fine-Patterning on Glass Substrates by the Sol-Gel Method, Journal of Non-Crystalline Solids, **100**, 501 (1988)
35. K. Heuberger, W. Lukosz, Embossing technique for fabricating surface relief gratings on hard oxide waveguides, Appl. Opt., **25**, 1499 (1986)
36. W. Lukosz, K. Tiefenthaler, Embossing technique for fabricating integrated optical components in hard inorganic waveguiding materials", Opt. Lett., **8**, 537 (1983)
37. J. L. Noguès, R. L. Howel, Fabrication of pure silica micro-optics by sol-gel processing, Proc. of SPIE "Miniature and Micro-Optics", **1751**, 214 (1992)
38. M. Mennig, A. Gier, H. Krug, H. Schmidt, Preparation of micropatterns with profile heigths of up to 30 μm from silica sols, SPIE "Sol-Gel-Optics IV", volume **3139**, 480 (1997)
39. A. Gier, Diplomarbeit, Universität des Saarlandes, Germany (1996)
40. M. Mennig, G. Jonschker, H. Schmidt, Sol-gel-derived thick coatings and their thermomechanical and optical properties, SPIE "Miniature and Micro-Optics", volume **1758**, 238 (1992)