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Micro structuring of inorganic glass by hot embossing of coated glass wafers

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Abstract

Hot-embossing is an economical manufacturing process for the structuring of glass. However, this process is limited by the sticking of glass melts on the moulding tools. In order to prevent this problem, the glass substrate was coated with thin metal, carbon and oxide layers. In the current work the behaviour and suitability of the coatings for the embossing process were investigated. As a result it was found that all coatings showed a clear decrease of the adhesive forces and an increase of the sticking temperature out of the range relevant for hot embossing. The examined coatings behave ductile, however, under larger elongations they tend to cracking. Examples of fluidic structures with lateral geometries in mm and µm range were realized. The coatings could be successfully applied in moulding experiments without reduction of the quality of the embossed structures by sticking of the glass melts. The largest aspect ratio of embossing depth to structural width amounted to 3.

Introduction

The material glass plays an important part in many applications of micro system technologies. It offers a high thermal stability, chemical durability as well as a wide variation of refractive indices in comparison to polymers (Katsuki 2006). Furthermore, inorganic glasses do not show ageing. For micro-fluidic applications the possibility of surface functionalisation, good fluorescence characteristics, the high mechanical strength, the good mechanical stability as well as some dielectric properties are advantageous. The latter permits to construct electrokinetic fluid actuators. Due to its biocompatibility biological chips on glass substrates are possible (Khan-Malek et al. 2007; Tay et al. 2006). With respect to optical applications, the variable refractive indices, combined with a very small light absorption allow a compact design of optical components. Hence, the realization of new optical layout conceptions as well as the integration of optical and mechanical functions (Brinksmeier et al. 2004; Yan et al. 2009) is feasible.
The micro structuring of glass by forming processes based on viscous flow of glass melts at high temperatures permits a cost-efficient production of microelectromechanical system (MEMS) components.
Especially in respect of batch-based manufacturing is it necessary to qualify a production technology for flat glass on wafer level base (Schubert et al. 2006). One of the problems associated with the hot embossing of glass is the contact behaviour between the mould and the hot glass melt. If the process is carried out at too low viscosities i.e. too high temperatures, adhering or sticking of the glass to the mould surface occurs. This might lead to a damage of the glass or the mould (Klocke and Pongs 2004). If the process is carried out at lower temperatures, where the viscosity is notably larger, the necessary mechanical forces are too large to enable a fast production process. To overcome this problem, it was tested to decouple the glass viscosity from the sticking behaviour. For this purpose the forming moulds were coated, which showed, however, only limited success and brought satisfying results only when using the classical glass pressing process (Rieser 2004). A shift of the sticking temperature in the

isothermal hot embossing process to lower viscosities was not observed (Rieser et al. 2007). The high strains for the production of microstructures with high aspect ratios require lower viscosities during the pressing procedure (Hock et al. 2003). Low viscosities are necessary in order to complete the pressing operation in a reasonable process time with moderate pressing forces. To prevent these problems, a new coating strategy was developed. It aimed at the decoupling of the viscosity in the glass volume from the sticking behaviour at the glass surface. In contrast to the approaches described above, not the mould, but the glassy substrate was coated (Edelmann et al. 2008). The new coating-strategy has many advantages: For every hot embossing operation, the same parameters can be applied since there is no abrasion of the coating layer. The requirements to coat flat glasses are much lower than to coat a complex mould. Furthermore, the coating of float-glass is state of the art.

Experimental procedure

Substrate and Coatings

As substrates, 50 mm diameter wafers of 1.6 mm thick soda-lime and 1 mm borosilicate float glass were used.

The investigated coatings are amorphous carbon, metallic coatings of chromium and gold as well as oxide coatings of TiO_2 and SiO_2. The metallic coatings were deposited by PVD-processes with a thickness range of 10 – 50 nm. The carbon coatings were evaporated from vacuum with a thickness of 50 nm. For the TiO_2 and SiO_2 coatings, sol-gel processes were used. Furthermore a Combustion-Chemical-Vapour-Deposition (CCVD) process was used for the preparation of silica layers. The thicknesses of all oxide coatings were in the range from 40 to 100 nm.

Before coating, the glasses were cleaned and dried. The samples were emerged in a cleaning liquid for 10 min at 65°C in a ultrasonic bath to remove dirt and fat from the surface. Afterwards they were rinsed with distilled water and placed again in the ultrasonic bath for another 10 min. Subsequently the samples were dried at 100°C.

The gold coatings were deposited by sputtering (by the Institute for Applied Physics of Jena University, Germany) and the chromium coatings by a PVD

process (by the INOVAP Innovative Vakuum- und Plasmatechnik GmbH, Dresden, Germany). The carbon coatings were prepared by evaporation in vacuum (Edwards Auto 306 from Edwards Hochvakuum GmbH, Marburg, Germany) at 1 x 10^{-6} mbar for 1 s and subsequent resublimation.
For sol-gel coatings, a dip-coating process was used. The precursor for the TiO_2-coatings is tetraisopropyl-orthotitanate (TPOT) and for the SiO_2-coatings tetraethyl-orthosilicate (TEOS). The composition of the TiO_2-sols was: 39.62 ml TPOT, 157.06 ml Ethanol, 2.43 ml H_2O and 0.89 ml HCl. For the SiO_2-sols, the composition was: 60.8 ml TEOS, 125.3 ml Ethanol, 29.33 ml H_2O, 3.04 ml CH_3COOH. Before use, the SiO_2-sol was aged for 2 days. To perform different film thicknesses, the drawing speed was varied in the range of 5 to 15 cm/min. After coating, the samples were dried for 30 min at 100°C and subsequently calcined for 30 min at 500°C.
The CCVD process was performed with a commercial flame coating device (Pyrosil® Flame coating device GVE from SURA Instruments GmbH, Jena, Germany). The burner is mounted on a linear motion unit (from Jenaer Antriebstechnik GmbH, Jena, Germany). During the experiments all parameters, such as gas pressure, burner distance from the substrate and the burner velocity were kept constant. The pressure of the carrier gas was 1 bar, the burner velocity was 100 mm/s and the distance between the burner and the substrate is 7 mm. For the experiments 10 coatings were performed.
The samples were characterized by scanning electron microscopy (SEM), optical microscopy and laser-scanning-microscopy (LSM).
The topography and roughness were measured by LSM. From the reflection of the laser, intensity profiles (IP) were recorded. The difference in the intensity of the reflected laser results from different material contrasts and surface structures. In addition, optical differential interference contrast (DIC) micrographs were realized. DIC works on the principle of interferometry to gain information about the optical density of the sample, to see otherwise invisible features, especially with the transparent coatings.

Experimental equipment

A process chamber, which is integrated into a precision press equipment, forms the experimental set-up for glass hot-embossing at the Fraunhofer IWU. It serves

as mounting for the die system, medium supply, as well as the sensors for process control. Positioning and load transmission are realized by the precision press equipment. For accurate hot embossing of the microstructure on a flat substrate, an exact controlling of the mould path is necessary. To satisfy these requirements, the press is equipped with four spindles and four synchronized servo-drives. The process set-up is shown in Fig. 1.

With this set-up a precise isothermal tempering can be ensured at forming temperatures up to 1000 °C. The temperatures are separately adjustable for the upper and the lower mould with a deviation of 1 Kelvin. The present structure of the tool system enables heating and cooling rates of 25 K/min. Significantly faster temperature changes do not seem meaningful due to the absolutely necessary isothermal tempering conditions. However, in combination with an additional preheating station process times of a few minutes could be realized.

With this testing set-up embossing forces up to 50 kN on a wafer of 50 mm diameter can be applied. To avoid oxidation as well as to assure a complete form filling of the microstructures, it is possible to work either within a vacuum range of 1×10^{-3} mbar or under inert gas atmosphere.

Determination of adherence and sticking behaviour

For reference first, the adherence and sticking of an uncoated substrate was studied by a reproducible test sequence with an unsophisticated plane pressing mould of the high-temperature tensile material TZM (Titanium-Zirconium-Molybdenum). This material has a very high melting point, a low thermal expansion coefficient and a high thermal conductivity that makes it an ideal material for glass forming dies.
The adhesion of glass to the mould in the hot embossing process depends on several process parameters, from which the temperature and thus the glass viscosity has the largest effect. The practice-relevant process parameters, such as pressing power (10 bar), time of contact (60/120/180 s), inert gas pressure (5 mbar argon) were kept constant. The embossing temperature was increased gradually, until the sticking phenomena occurred, which means that the tool and the glass could not be separated any longer without destruction. This temperature will be

denoted in the following as sticking temperature. The statistically reproducible adhesive forces occurring at lower temperature were determined. Both, the sticking temperature and the adhesive forces served afterwards as comparison criterion for coated glasses.
With the coated glass samples hot embossing tests were accomplished using the same conditions where sticking with the uncoated samples occurred. When the adhesive forces had decreased, the temperature was again gradually increased up to the softening point of the glass. The use of higher temperatures in hot embossing is not expedient, due to the fact that the glass would continue to deform after the forming process.

Ductility test

In order to determine the effects of the deformation of the coatings, it is advantageous to realize different strains with the same process conditions. Therefore, a flat TZM-tool with a diameter of 43 mm was used. Holes of 0.5 mm diameter have been drilled in the surface. The geometric arrangement of the holes is shown in Fig. 2. Pressing this round flat mould on a glass results in a drop of the pressure from a maximum in the centre to a minimum in the periphery. The glass flows into the holes increasing its surface whereby in each hole almost spherical lenses are formed. Following the surface growth the coating on the glass is stretched differently, depending on the pressure distribution from outside to the centre of the wafer. Hence, in one hot embossing experiment different layer elongations can be realized.
An embossing impetus (product of pressing force and duration of action) was chosen that the height of the formed lens resulting in the centre corresponds to the half of the hole diameter (height of A = 250 µm).

Pressing of application structures

In order to study the possible changes in the coating structure at edges and along steep walls further embossing moulds were realized. Laser-structured silicon carbide moulds were used with micro fluidic structures and other characteristic shapes which were similar to an application structure.

The application demonstrator, a structured channel plate for a flow analysis system, is shown in Fig. 3. It exhibits a complex structure on a glass wafer in the size of a glass slide. The channel widths vary staggered from the left side of the part to the right from 500 µm to 753 µm, since fluid is added at 12 inlets in the analysis system but the flow of the fluid, which should be analyzed, is to be kept constant. The channel depth of 100 µm is kept constant over the entire structured surface. The structure has been eroded with sloping edges, hence the channels at the bottom were narrower than at the top. The flank angle of the channels approximate 110°.

Results

Adherence and sticking behaviour

The critical sticking disposition of an uncoated soda-lime-float glass was found at a temperature of 680°C ($\eta = 10^{8,5}$ dPa*s) and for Borofloat® at a temperature of 720°C ($\eta = 10^{9,2}$ dPa*s).
In Fig. 4 the influence of the coatings on the adhesive forces and the sticking temperature is presented.
It was verified by the experiments with all examined coatings, that the sticking temperature of the coated samples is shifted near to the Littleton-point of the glass. The adhesive forces could be reduced to less than 10%, compared with the uncoated glass.

Coating expansion in the ductility test

A typical hot embossing sample prepared by the ductility test is shown in Fig. 5 together with the mould. It can clearly be seen that the glass has flown into the holes and formed spherical lens shapes. Table 1 shows a summary of the average height of the mouldings resulting from the ductility samples with different coatings depending on the radius of the relevant holes.

Table 1: Average height of the hot embossed mouldings using the ductility tool

Radius (centre to periphery) / Coating	A	B	C	D	E
	height [µm]				

without (theoretical)	250	245	215	170	80
gold	245	236	205	180	101
carbon	239	212	187	146	102
SiO_2 (CCVD)	240	235	216	180	90
SiO_2 (sol-gel)	259	245	195	150	80
chromium	250	231	218	146	100

The height of the mouldings decreases from the middle of the sample (A) to the border (E). The height of the respective forming equates to the theoretical height. The deviation of the height at the same radius of one sample was less than 10%. Within the measurement deviation, the roughness (measured with LSM) of the mouldings is nearly the same and was quantified by 0.14 µm ± 0.05 µm.

The carbon coatings show small cracks at low deforming degrees. At higher deforming degrees, the cracks are larger and the layer is forming a soil like surface. Further deforming caused a growth and a proliferation of the cracks; hence the soils were getting smaller.
Fig. 6 shows intensity profiles of the coatings at the middle of the moulding are presented. The left picture shows a carbon coating at the middle of the ductility sample (A), which is attributed to the highest deforming degree. The dark cracks and the bright layer soils can clearly be distinguished. In the right image (radius E), some smaller cracks in the coating with few branching are visible.

A similar behaviour could be found with the chromium coatings. However, the cracks are thinner and the complete net is more branched, showing smaller soils in comparison to the carbon coatings.
With small deforming degrees, also the TiO_2 (sol-gel) coatings showed fine cracks. In the range of higher deforming degrees, the cracks initially grow, then the crack width remains approximately constant, while the quantity and branching of the cracks increase. Fig. 7 shows a DIC-micrograph of a TiO_2-coating with highly branched cracks, which results from a high deforming degree in the middle of the ductility sample (B).

The SiO_2 coatings, deposited by the CCVD process are faultless at the outer radius (E). But with higher deforming degrees cracking of the coating can be found which are similar to the TiO_2-coatings. Higher deforming degrees result in an increase of crack branching.

The SiO_2-coatings, deposited by the sol-gel method, showed completely different crack behaviour. In comparison to the other coatings, the cracks are approximately perpendicular to the radius of the lens. The higher the deforming degree the larger number of cracks could be observed.

A typical SEM-micrograph of a moulding with a SiO_2-sol-gel coating at medium deformation degree (D) is presented in Fig. 8. The coating layers appear like a thin skin with the coaxial cracks aforementioned. The deviation of the edge from a theoretical circle results from the geometry of the hole.

The ductility tests of gold coatings results in a change of the surface structure. These changes were caused by an evaporation of the gold but not by the forming process.

Table 2 shows the valuation of the coatings after the ductility test. The numbers illustrate the failure of the coatings corresponding to the expansion. The increasing number represents a higher failure. The coatings of chromium and gold show the lowest failure and the TiO_2-coatings were marginally worse.

Table 2: Damage of the coatings at different elongations

Radius	Elongation [%]	coatings					
		gold	carbon	SiO_2 (sol-gel)	TiO_2 (sol-gel)	SiO_2 (CCVD)	chromium
A	50	III	IV	IV	III	III	III
B	49	II	IV	IV	III	II	II
C	43	II	IV	III	II	II	II
D	34	I	III	II	I	I	I
E	16	I	I	II	I	I	I

explanation	IV - heavy damage of the coating	II – low damage of the coating
	III - medium damage of the coating	I - no/marginal damage of the coating

The geometry and the accuracy of the formed lenses, determined with LSM and SEM, correspond to the used tool.

Embossing of micro fluidic structures

The application structure for a flow analysis system was hot embossed in soda-lime float glass coated with SiO_2 (CCVD), carbon or chromium. The basic embossing parameters resulted already in a very good replication quality, however with several edge breakouts at small radii of the channel structure. The attempt to decrease these breakouts by an extended relaxation time was not satisfactory. Glass breakouts were indeed no longer observed, however, the adhering forces between tool and glass induced a warping of the structure after embossing.

For the determination of the necessary embossing impetus the complete replication of the structure within a test series was accomplished. Here, the embossing impetus was slowly increased, until a complete filling of the structure was reached, i.e. the tool structure was completely embossed without any shape distortion as shown in Fig. 9.

Fig. 10 shows two embossing results with different impetuses. On the upper image clearly a still strong shape distortion between channel structure and embossing level can be observed. The channel of the desired application structure does not possess a rectangular cross section, which could lead to leakages between two channels. However, the sample on the lower image shows a completely transferred structure. The embossing impetus was approx. 40% higher in comparison to the sample on the upper figure along with otherwise unchanged embossing parameters. With the optimized process parameters the application structure could be hot embossed defect-free.

The topography of the embossed cavity, with respect to the complete moulding and the reliable replication without a disruption of borders, is shown in Fig. 11. The bright part in Fig. 12 represents a polished cross-section of a moulded channel. During the sample preparation, some spalling at the borders may exist. The dark area in the middle of Fig. 12 results from a tilt of the sample.

Table 3: Flank angle of the embossed glass structure measured in the polished cross-section

	carbon	**SiO_2 (Sol-Gel)**	**chromium**
depth [µm]	107 ± 4	104 ± 4	102 ± 1
angle left [°]	121 ± 5°	114 ± 7°	110 ± 3°
angle right [°]	108 ± 4°	110 ± 4°	111 ± 1°

The measured parameters of the polished cross-section are shown in Tab. 3. The desired embossing depth is obtained within the allowed tolerance range. The angles at the borders correspond with the geometry of the applied mould.

Discussion and Conclusion

Isothermal hot embossing of coated glass wafers enables to mould functional structures of micro system technology in a reliable manufacturing process. For exact structure replication, the obstructive sticking effects can be minimized by coating of the flat glass substrate. The sticking temperature of the coated glasses is even higher than the temperature process range, which is feasible for micro structuring. Generally, all examined coatings can be used to prevent the sticking of the glass in the hot embossing process.

In a certain range, all coatings are ductile. However, at larger deformation degrees, the coatings fail, usually in form of cracks. This does not necessarily lead to an impairment of the embossing i.e. the forming process. The chromium, gold and SiO_2 (CCVD) coatings shows the least failure. However, the other coatings could not be excluded from further research, due to the fact that the effect of the adherence and the sticking is not yet clarified, which has to be a matter of following research. If the coatings, in spite of failure, prevent the sticking, it should have no influence for the most applications. After the forming process it is

possible to remove the non-oxide coatings, hence no limitations of the applications are to be due. Because of their chemical and physical properties, the oxide coatings were not obstructive for microfluidic applications. The influence of the coatings on optical applications is subject of further investigations.
The deviation of the height of the moulded lenses from the theoretical one (shown in Tab. 1) can be explained by a tilt of the tool.
The experiments demonstrate that the best replication of the structures requires to use a process with a very narrow field of process parameters. The sole adjustment of one parameter, such as pressing temperature (i.e. moulding viscosity) or the relaxation time, does not necessarily result in a better accuracy of the shape after embossing. The structures can be moulded defect-free and with high accuracy, if the process parameters are optimized. The measurement and the comparison of the moulded structures with the mould shows, that the quality is limited by the shape accuracy of the moulding tool.
The coating of the glass enables to use the hot embossing at high shear rates and at low viscosities. This has a positive effect to the accurate reproduction of surface details as well as the cycle time for embossing. Furthermore, the deleterious internal stress in the glass will be strongly reduced during hot embossing.
By contrast, machining and erosive manufacturing methods cause rough surfaces, impair the glass at the machining unit and often require a finishing (Belloy 2002 et al.; Lim 2004). Analogous limitations were considered for etching processes. However, they were constrictive to special photo structurable glasses (Schubert et al. 2006; Tay et al. 2006). These processes are economically justifiable for prototyping and small series.
Other moulding processes, such as precision moulding or micro hot embossing are available for small, single optical components, e.g. one-side spherical and non-spherical lenses. These processes are limited for few special glasses, requires expensive and difficult machinable moulding materials (cemented carbide, ceramics) with non-sticking tool-coatings (Klocke et al. 2004; Takahashi et al. 2007; Hock et al. 2003; Schubert et al. 2006). By contrast, the new coating strategy enables the structuring of glasses with high sticking affinity, such as borosilicate glass and expands the range of tool materials.
With hot embossing of coated glasses, the manufacturing of high extensive geometries in µm-range for large-scale micro structuring of inorganic glasses is

possible. This technology enables a higher vertical range of manufacture for the glass industry. Hence, not only preformings, but also complete components can be provided.

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Figure captions

Fig. 1 Process chamber for hot embossing of glass

Fig. 2 TZM Ductility tool (above) and the geometric hole design (bottom)

Fig. 3 Laser structured SiC embossing tool with micro fluidic application structure

Fig. 4 Influence of the glass coating on adhesion forces and sticking temperature in the hot embossing process

Fig. 5 Presentation of a the ductility tool and an embossed sample

Fig. 6 Intensity profile of the middle of a carbon coated moulding; left: high deforming degree at center, right: low deforming degree near the periphery

Fig. 7 DIC-micrograph of a TiO_2-coating showing a high dgree of deforming

Fig. 8 SEM micrograph of a moulding with an SiO_2-sol-gel coating with medium deformation degrees

Fig. 9 Embossed micro fluidic structure

Fig. 10 Detail of the channel structure at different embossing impetuses

Fig. 11 Topography of a hot embossed channel structure

Fig. 12 Micrograph of a polished cross-section of a moulded channel