

Preparation of micropatterns with profile heights up to 30 microns from silica sols.

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ABSTRACT

A new synthesis and processing route for SiO₂ glass like micropatterns with heights up to 30 µm by gel embossing and thermal densification has been developed. For this reason an organically modified nanoparticulate sol prepared by acid catalysis of methyl- and phenyl- triethoxysilane and tetraethyl orthosilicate in combination with colloidal silica sol was used. Sol coatings with thicknesses up to 15 µm are obtained by dipping of float glass substrates. After a predrying step of about 60 s micropatterns are obtained using a pressure of only 2.5 mN/mm². Due to this low pressure, flexible and low cost silicon rubber stampers can be used. The gelation time of the sol can be extended from 5d to 16 days and the working time for embossing can be extended from 60 s up to 100 s by a partial replacement of methyl silane by phenyl silane from 0 to 20 mole %. After embossing and drying at 50 °C the patterned layer was densified at temperatures up to 500 °C to 95 % density as indicated by refractive index measurements. It is assumed that the densification process is strongly promoted by the used colloidal silica nano particles. The linear shrinkage of the micropatterns is limited to about 25 % due to the high solid content of the sol and the high green density of the layers. Since the structures are densified at temperatures far below T_g sharp edged patterns can be obtained as shown by high resolution secondary electron microscopy.

The capability of this technique is demonstrated by the fabrication of light trapping structures with pyramids of 7 µm in height and 10 µm in width on an area of 20 x 20 mm² and micro lens arrays of lenses with 30 µm in height and 600 µm in diameter on an area of 20 x 30 mm².

Keywords: sol-gel, embossing, micropatterns, colloidal silica, solar cells, light trapping, micro lens arrays

1. INTRODUCTION

In the recent years, the field of micro-optics has gained increasing interest. The need to control and manipulate light on a microscopic scale has driven optical engineers to seek new fabrication methods that will provide cost effective and unique solutions without compromising quality and performance. Optical components such as relief gratings, pyramidal structures for light trapping and micro lens arrays are typically fabricated by etching and lithography [1], ion exchange [2, 3] or embossing [4, 5]. For embossing mostly organic-inorganic hybrids have been investigated. The combination of the organic-network and the inorganic components causes a very low shrinkage and therefore film thickness of about 30 µm. Structures like wave guides with 10 µm x 10 µm crosssection and 5 cm in length and micro lens arrays on an area of 4 cm x 4 cm (amplitude of 30 µm) and relief gratings with 3600 lines/mm (amplitudes of 10 µm) have already been fabricated [4,5].

Such structures with dimensions of up to 30 μm in height are promising for light trapping structures in photovoltaic applications. But with respect to high temperature processing the described hybrids are not suitable. For CdS/CdTe- or for amorphous Si-cells temperatures of up to 550 $^{\circ}\text{C}$ are required for the densification of the corresponding layers [6]. Furthermore better chemical resistance and improved mechanical properties like scratch resistance could be helpful.

Inorganic silica or silica titania films prepared by 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 glass-like materials used for micropatterning by embossing show two main disadvantages. The films shrink about 60-70% vol% after densification, so that a near net shaping is not possible. Furthermore the thickness is limited to 80-200 nm and the embossing depth obtained by this technique is extremely low [7-11].

The height of the embossed structures is limited due to the critical thickness of about 1 μm of the glass like coatings. The critical film thickness is determined by the tensile stress in the film which results from the shrinkage during the drying and the densification step. This tensile stress leads to cracks in the film when the thickness exceeds a critical limit [12]. A methyl modified colloidal silica containing SiO_2 coating sol has been developed recently, which allows to produce crackfree and transparent SiO_2 coatings on soda-lime glass with a thickness of about 8 μm after densification at 500 $^{\circ}\text{C}$ [13]. The thickness of these layers was limited to 8 μm .

The aim of the present study was to prepare micro patterns with heights exceeding 10 μm on the basis of an optimized material with composition according to [13]. Therefore at first the embossing of the basic system had to be investigated and optimized with special respect to the working time for embossing of the wet gel film and the embossing pressure. Optimized coating materials key parameters are the sharpness of the edges, the shrinkage during drying and densification and the structural dimensions which can be achieved.

The chemical modifications of the basic system for optimization of the embossing process were focused on low cost and large area processing.

2. EXPERIMENTAL

For the sol synthesis methyltriethoxysilane (MTEOS), phenyltrimethoxysilane (PhTMOS) and tetraethyl orthosilicate (TEOS) were mixed in molar ratios of 80 : 0 : 20 (MTKS), 75 : 5 : 20 (5PMTKS) and 60 : 20 : 20 (20PMTKS) respectively. Colloidal silica sol (Bayer Kieselsol 300 / 30) with 30 wt. % of silica (particle radius about 7 nm) in water was added (67.7 g silica sol per mol alcoxide). Hydrolysis and precondensation were performed after adding 0.7 mmole HCl per g silica sol and rigorous stirring within 15 minutes. Finally the sol was filtered using a 0.8 μm disposable filter.

Float glass substrates (50 mm x 20 mm x 2 mm) were coated by dipping under cleanroom conditions (class 10000, air 15 ± 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 which was removed immediately after dipping.

Flexible stampers were prepared from different masters made from Ni, brass and Si using a silicone caoutchouc (sil gel, Wacker) by molding and drying at 50 $^{\circ}\text{C}$ for 5 minutes. After predrying of the coated gel films for 1...3 minutes at room temperature embossing experiments were performed. The caoutchouc stampers were placed on a cylinder of about 3 cm in diameter and 10 cm in length and deposited on top of the gel layer by rolling and simultaneous delamination from the cylinder. Afterwards the stamper was loaded by a weight yielding to a pressure of 2.5 mN / mm^2 . After embossing time of 10 minutes at 50 $^{\circ}\text{C}$ the stamper was removed and the film was dried at 100 $^{\circ}\text{C}$ for 30 minutes and then heated to 500 $^{\circ}\text{C}$ with a rate of 5 K / min. This temperature was held for 60 minutes and then the samples were cooled down to room temperature within 10 h.

The viscosity of the sol was measured as a function of aging time using a rotation viscosimeter (Pysica; rheolab MC 120). The morphology of the micro patterned glass like coatings was investigated by profilometry, light microscopy and high resolution scanning electron microscopy (HR-SEM).

3. RESULTS AND DISCUSSION

In order to obtain embossing results to be evaluated with respect to the usefulness of the materials for the embossing process, a reliable and simple technique had to be developed. In order to be able to emboss larger areas very simply a flexible copy of masters had been fabricated from conventional masters made from Si, Ni and brass. In fig. 1 the whole process is shown.

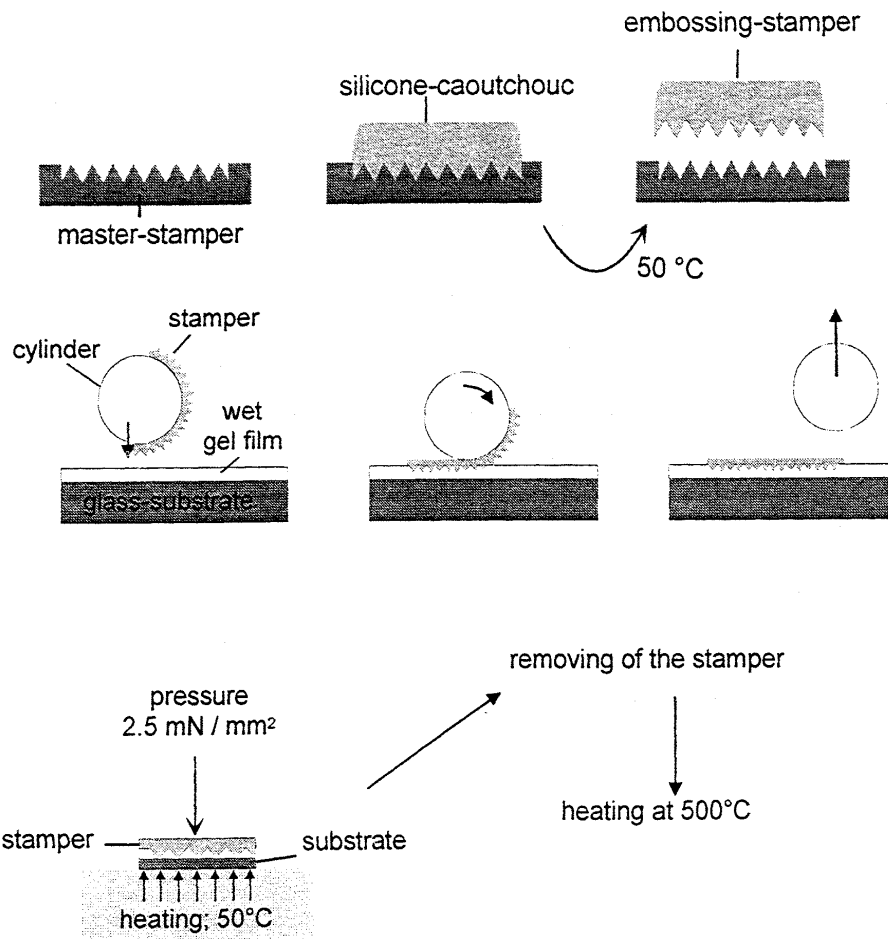


Fig. 1: Schematic representation of the embossing and the densification process.

The use of the silicone rubber was possible, since the usual gel showed a viscosity, low enough to be embossed with the soft stamper, which might be advantageous for large area embossing.

In order to determine the parameters for the synthesis and the embossing steps with special focus on a reproduceable preparation of sharp edged micropatterns on an area of 20 x 20 mm², stampers with parallel prisms of different heights (35 ... 40 μm, base 120 ... 150 μm) were used. The predrying time (intervall between dipcoating and embossing) was varied and the quality of the embossed gel was evaluated by microscopy, which lead to the following results.

Sol layers prepared only from MTEOS, TEOS and colloidal silica sol (MTKS) but without PhTMOS gelled rapidly. The predrying time could only be varied between 60 ... 75 s. Times shorter than 60 s lead to fade structures, after longer predrying the layers were already too hard for embossing with the flexible stampers. In order to extend the working time, MTEOS was partially replaced by PhTMOS. For a replacement of 5 mole % of MTEOS by PhTMOS (5 PMTKS) the working time could be extended to 60 ... 85 s and for 20 PMTKS layers it was extended to 60 ... 100 s.

Therefore it was possible to obtain embossing by a viscous flow of the sol before gelation. The pressure required for this process of about $2.5 \text{ mN} / \text{mm}^2$ is about 3 orders of magnitude lower than for the embossing of gels from TEOS sols [7, 8]. The use of a flexible stamper is very important for large area applications on glass substrates with uneven surfaces.

The partial replacement of MTEOS by PhTMOS had also a remarkable influence on the shelf life of the sol as one can see from fig. 2.

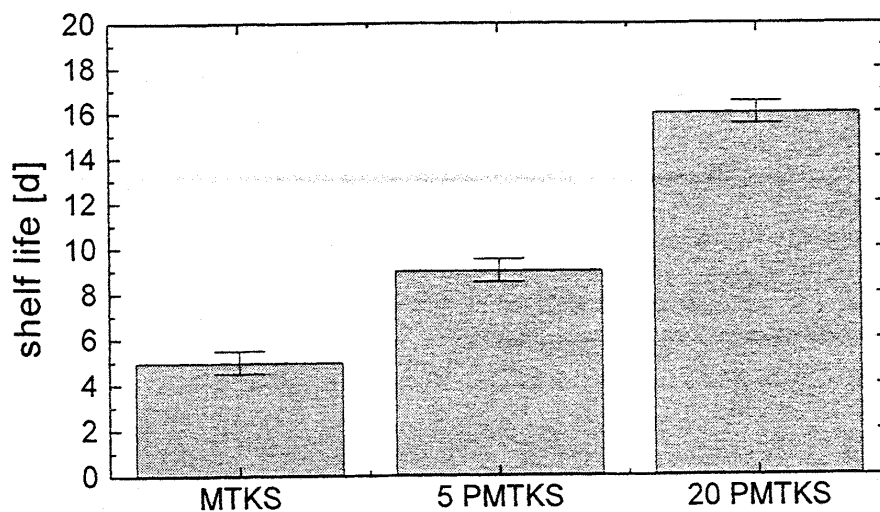


Fig. 2: shelf life of sols with different PhTMOS contents determined from viscosity measurements as a function of the aging time

It shows the shelf life, determined by viscosity measurements, using a maximum viscosity of 1 Pa s to determine the shelf life. Fig. 2 clearly shows that the shelf life significantly increases with the PhTMOS content in the investigated concentration range.

It can be assumed that the gelation of the sol by 3-dimensional crosslinking is slowed down due to the larger volume of the phenyl groups compared to the CH_3 -groups of the MTEOS.

In order to investigate whether micropatterns obtained from these organically modified SiO_2 sols could be converted to a defect free glass like material, the following experiment was carried out. A $20 \times 20 \text{ mm}^2$ part of a plastic record was used as a master and a silicone stamper was prepared from it and used for embossing (see fig. 1). The record was chosen as a low cost master with structural heights up to $40 \mu\text{m}$ (depth of the tracks). The so obtained replica of the record was densified at 500°C and monitored by HR-SEM together with the master, which is shown in fig. 3.

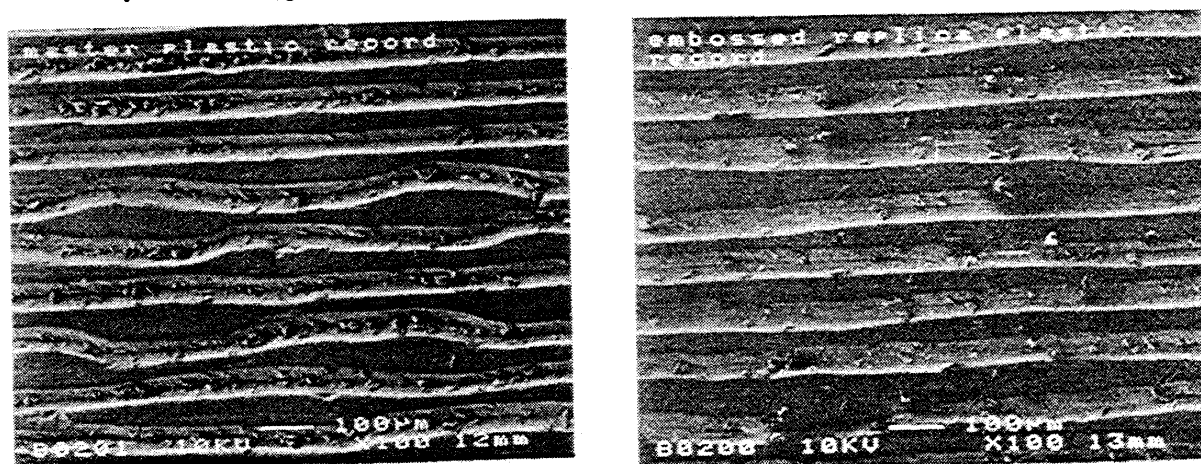


Fig. 3: HR-SEM picture of a plastic record (left) and an embossed replica of it (right) after densification at 500°C .

As one can see from fig. 3 a sharp edged, crackfree replica of the record could be obtained. The pattern of master and replica are similar. The structural height was determined by profilometer to be about 30 μm . The pattern appears clear and transparent, inclusion of carbon cannot be detected visually or by microscopy. The inclusion of gas bubbles could be avoided by the rolling technique (see fig. 1). Furthermore it is assumed that ethanol vapour, generated during the gelation at 50 $^{\circ}\text{C}$ can penetrate through the silicon rubber stamper easier compared to Si- or metal stampers.

Comparing structural height of embossed samples before and after firing by profilometer it was found that the shrinkage in height during firing is about 25 % which is much lower than for micropatterns from TEOS gels (60 ... 70 % [8]). The low shrinkage is due to the rather high SiO_2 content of the sol (296 g / l) and due to the fact that the methyl and the phenyl groups are burned off for temperatures in the range between 550 $^{\circ}\text{C}$... 600 $^{\circ}\text{C}$ [14].

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, obtained from refractive index measurements [13]) after firing at 500 $^{\circ}\text{C}$.

For further investigations stampers from different materials (Si and brass) and with different geometries were used. Fig. 5 and fig. 6 show micropatterns of appropriate replicas (after densification at 500 $^{\circ}\text{C}$) with pyramidal (fig. 4, Si-master) and hexagonal (fig. 5, brass master) structures with heights between 7 μm (fig. 4) and 30 μm (fig. 5) and lateral dimensions between 10 μm (fig. 4) and 600 μm (fig. 5).

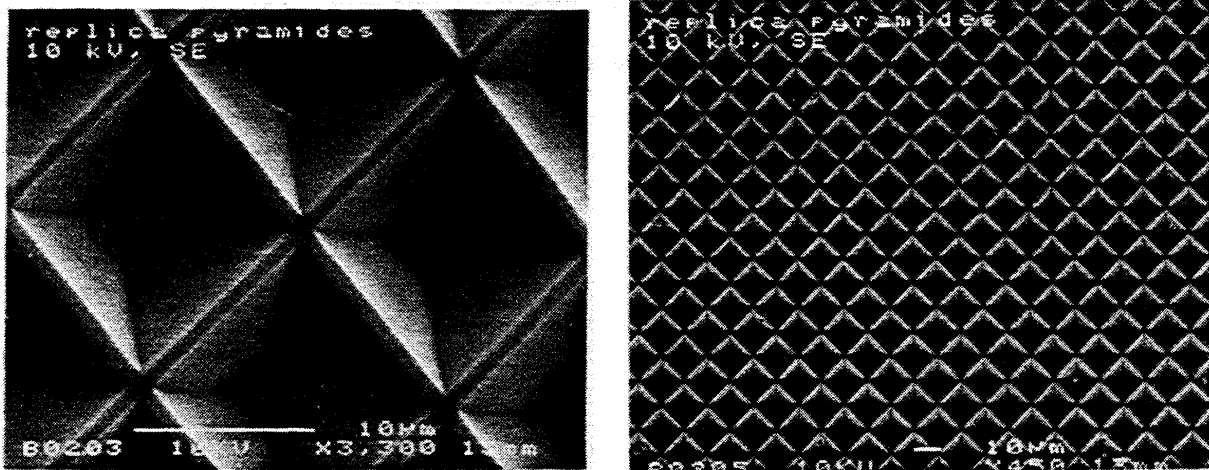


Fig. 3: HR-SEM picture (left picture with tilt 20 $^{\circ}$) of an embossed pyramidal structure after densification at 500 $^{\circ}\text{C}$

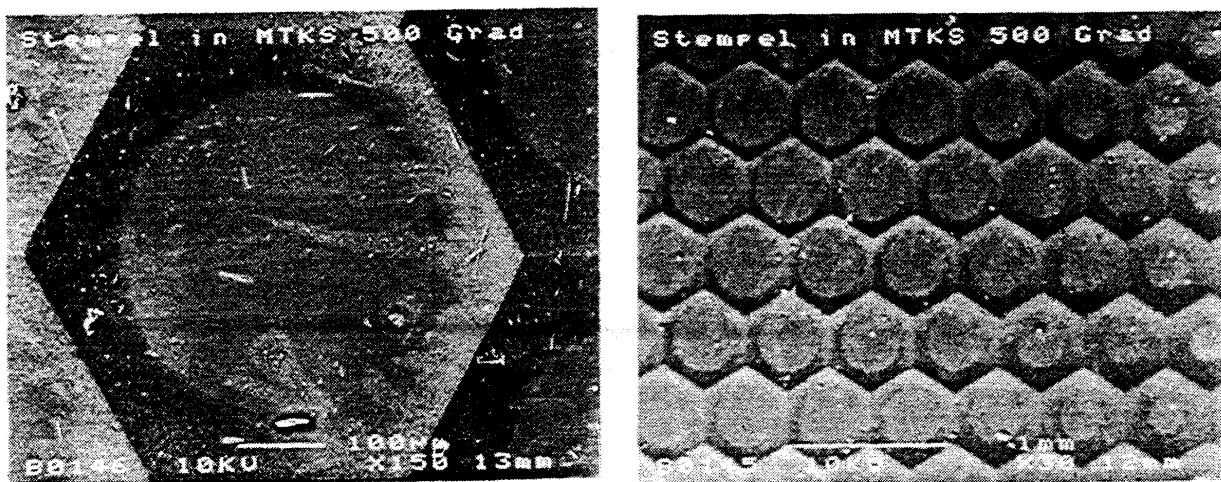


Fig. 4: HR-SEM picture of an embossed hexagonal structure after densification at 500 $^{\circ}\text{C}$.

Such patterns were obtained on areas up to 20 x 30 mm². This limit is due to the dimension of the master stamper but not due to material properties or demands from the embossing process. The pattern in fig. 6 was generated from a brass master with relatively high surface roughness, which is replicated in the micropattern, as one can see from fig. 6.

On the other hand this indicates that the use of the silicon rubber stamper allows a great variety of master stamper materials, due to the low adhesion of the silicon rubber to many materials. Such patterns can be applied for light trapping of solar cells [6] (fig. 5) or micro lens arrays for UV laser applications (fig. 6). In both cases the glass like character of the micropatterns is required due to thermal and mechanical stability.

4. CONCLUSION

Soft gels have been developed, which are suitable for embossing with flexible stampers, using low embossing pressures. This is very important for the development of low cost large area applications and for micropatterning on substrates with uneven surfaces.

ACKNOWLEDGEMENTS

The authors thank R. Brendel from Max-Planck-Institut für Festkörperforschung (D-70569 Stuttgart, Germany), D. J. Werner from Institut für Physikalische Elektronik, Universität Stuttgart (D-70569 Stuttgart Germany) and AMS-Micro-Optics company (Germany) for the preparation of the stampers, Th. Krajewski (INM Saarbrücken) for the HR-SEM investigations and the Federal Ministry of Research and Technology for the financial support.

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