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Fine patterning of thin sol–gel films

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An embossing technique was used to fabricate surface reliefs in organically modified ceramics of the Ormocer type, synthesized via the sol–gel route. Embossing techniques for these materials are described and results of embossed grids and gratings with up to 2400 lines/mm and peak-to-trough values up to 3 μm are presented.

1. Introduction

Integrated optical components such as waveguide gratings are typically fabricated by holography combined with ion milling [1] or direct electron beam writing [2]. These techniques are time consuming and expensive, so that mass production is ineffective. Because of numerous practical applications of such waveguide gratings such as planar waveguide couplers [3], beam splitters [4] and focusing elements [5], high production rates are worthy objectives. One approach to generate surface relief structures is embossing of sol–gel thin films, which offers a convenient alternative to vacuum methods. Embossing techniques for organic materials [6], for thin gel films prepared from organometallic compounds in solution and PEG-modified SiO_2/TiO_2 gels have been reported [7–10]. The sol–gel films are prepared by dip or spin coating and baked at 500°C. These films shrink 40–70 vol.% and a final film thickness of only 80–200 nm can be obtained. That means near net shaping is not possible. The optical loss of such SiO_2/TiO_2 waveguides is less than 1 dB/cm.

One of the problems with embossing inorganic gel layers is the thickness limitation and restricted plasticity. The embossing depth obtained by this technique generally is extremely low and not suitable to produce channel waveguides for multimode applications.

To overcome these problems, materials have to be developed which can be prepared with thicknesses up to 10 μm with sufficient softness during the embossing step, good mechanical properties after embossing and low optical loss. Therefore a concept of synthesizing inorganic nanocomposites was developed in order to minimize shrinkage by high nanoparticle packing [11,12].

2. Experimental

The coating material was synthesized from methacryloxypropyl trimethoxy silane (I), methacrylic acid (II) and zirconium-n-propoxide (III) precursors. A zirconium propoxide/methacrylic acid complex was formed by reacting the alkoxide with methacrylic acid. After addition of the silane (I), hydrolysis and condensation was performed by adding the appropriate amount of water to the mixture. A detailed description of the synthesis procedure is described elsewhere [11,12].

Films were fabricated by dip coating cleaned silica substrates using a withdrawal velocity of 5 mm/s. A viscosity of 17.1 mPa s was chosen. In order to avoid coating both sides of the substrate, one side was covered by a protective tape. A film of 3 μm thickness was obtained after drying in air for 1 min. Embossing and UV-curing was carried

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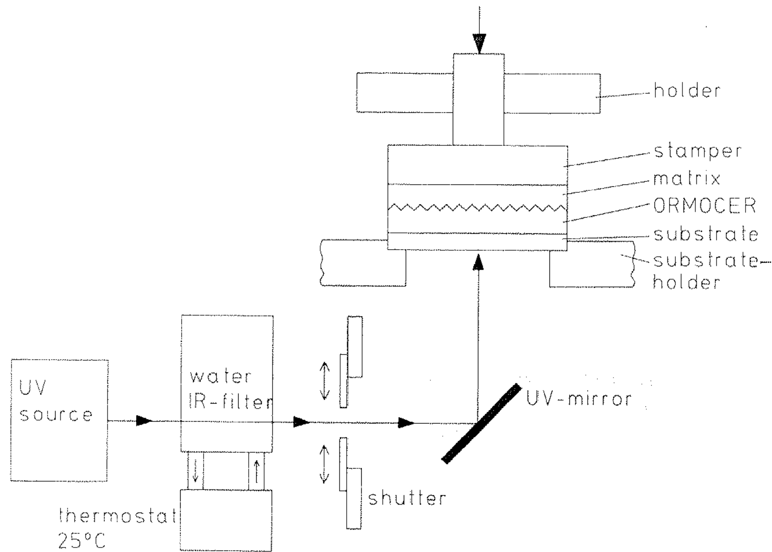


Fig. 1. Schematic apparatus for embossing in combination with UV curing.

out using the device shown in fig. 1. It includes a UV double beam source with a maximum adjustable total power consumption of 500 W, a water filter of about 10 cm length to remove IR, a shutter allowing control of the irradiation time and a UV-reflecting mirror.

A defined pressure between 10 and 100 N cm^{-2} was applied to the stamper which presses the deformable gel film against the master grating. After an embossing time of 10 min, the stamper was removed and the formation of the inorganic network in the layer completed by thermal treatment at 130°C for 1 h.

3. Results

The system described was chosen for several reasons. Compound (I) is commercially available and can act as a precursor to build a sol–gel-de-

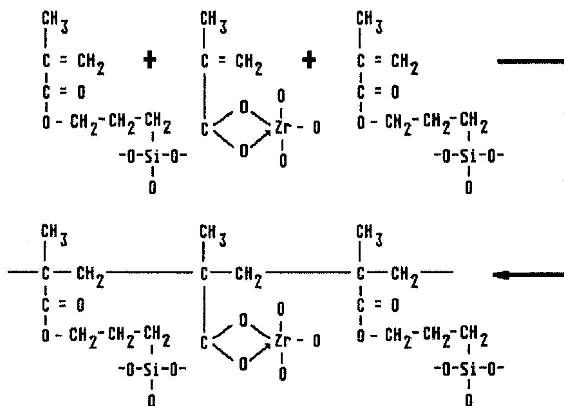


Fig. 2. Reaction scheme for the photocuring process.

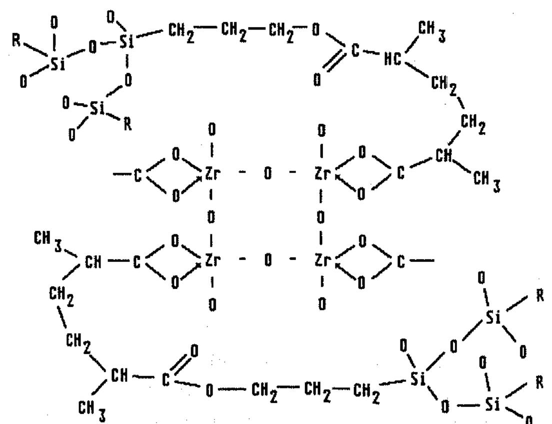


Fig. 3. Model for the 'ZrO_2' cluster formation.

rived inorganic backbone and, second, the methacrylate group can be polymerized with (II) to form organic chains. In addition, a chemical link to the inorganic network former Zr is attained by formation of a stable complex with (II) [12]. The inorganic component Zr in such systems provides a hard surface and high mechanical stability [13]. Moreover, addition of Zr increases the refractive index of such a composite [14,15], which should be greater than that of the fused silica substrates for optical applications. An inorganic network including Zr- and Si-containing units should be formed by hydrolysis and condensation. Direct formation of Zr–O–Si bonds seems unlikely from the chemistry of these elements. As shown in ref. [16], ZrO_2-containing clusters of 5–10 nm diameter are formed under these reaction conditions with complex bonds of methacrylic acid to Zr. The complex bond is stable under hydrolytic conditions [12] and thus provides a means of incorporating the ZrO_2-containing clusters into the matrix of silane(I) polycondensates by photopolymerization of the methacryloxy groups to the methacrylic ligands. The viscous liquid obtained by hydrolysis and condensation shows a surprisingly low shrinkage during densification (~ 5 vol.%), which is the basis for a near net shape embossing process. Polymerization takes place during the UV-initiated embossing step, as shown in fig. 2. The resulting nanocomposite can be considered as a 0–3 composite consisting of clusters connected by flexible units (fig. 3).

The build-up of the inorganic backbone takes place during the sol–gel synthesis, while the final polymerization takes place during embossing.

The refractive index of a system of the composition I : II : III = 10 : 1 : 1 (molar ratio) was determined to 1.52 (n_D). The optical loss of the films has been determined to 1 dB/cm at 632.8 nm, which is a promising starting value. Squared patterns with an edge width of about 10 μm and a grating with 2400 lines per mm have been prepared. In figs. 4(a) and (b), the SEM micrographs of the squared patterns are shown. The pattern is characterized by sharp edges and a high flank steepness. Film thickness is about 3 μm. Such structures can be used as transmission gratings.

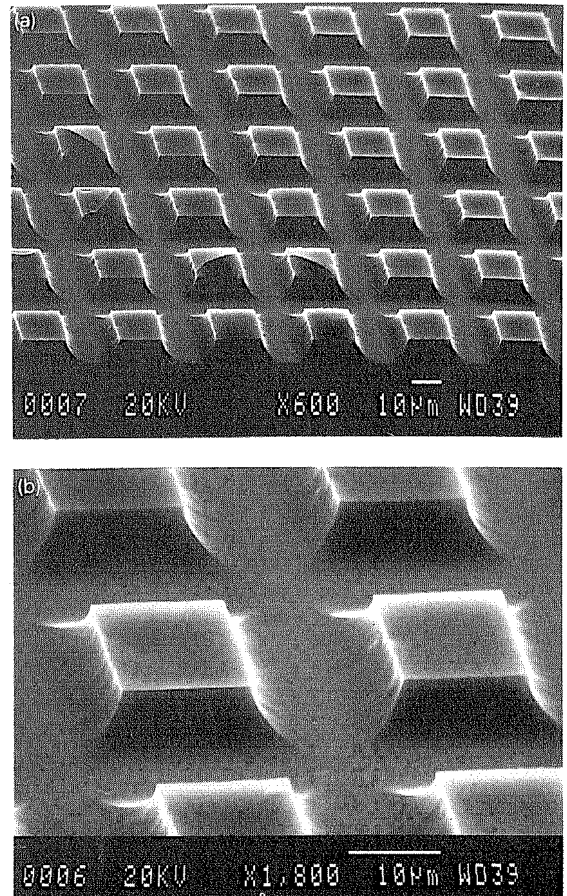
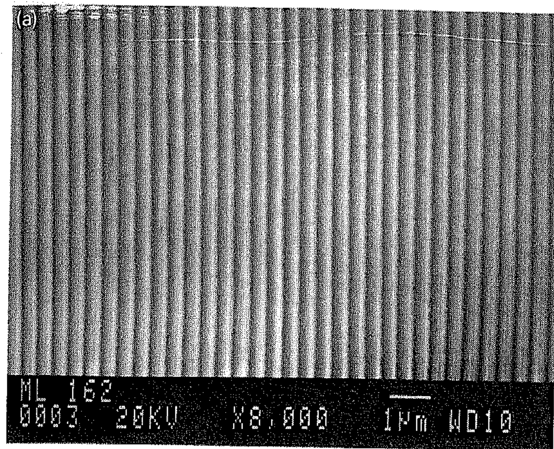


Fig. 4. (a,b) SEM micrographs of the embossed pattern generated by a grid.

Scanning electron micrography micrographs of the replica of a master reflection grating with 2400 lines per mm are shown in figs. 5(a) and (b). The embossed patterns show near net shape of the original sinusoidal surface of the stamper and demonstrate the ability of the system to reproduce fine lines exactly.

Low shrinkage is essential for near net shaping in case of high peak-to-trough values of some μm. As can be seen in fig. 4, peak-to-trough values of 3 μm are attainable for the composite materials. In principle, it is no problem to prepare films up to 10 μm and higher.

Some difficulties in the fabrication of the patterns are related to adhesion of the composite to



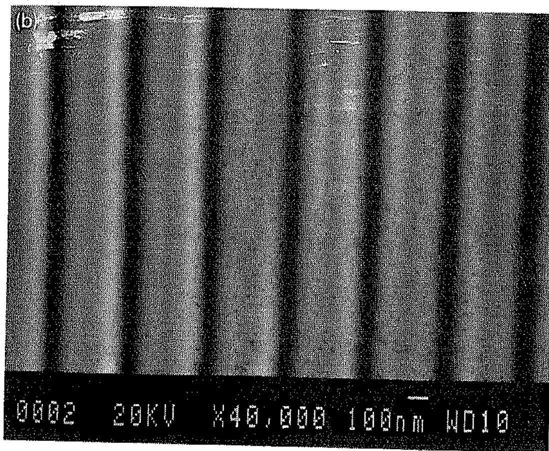


Fig. 5. (a,b) SEM micrographs of an embossed pattern generated by a commercially available reflection grating with 2400 lines/mm.

the stamper. Therefore proper coatings have to be chosen. For reducing the loss, which, at present is due to dust particles, clean room conditions must also be improved.

4. Conclusion

Combination of dip coating and embossing techniques permits good quality surface relief gratings to be fabricated. The index of refraction can be varied by the composition. The composite has low optical loss, synthesis-controlled homogeneity and low shrinkage which allows structures with peak-to-trough values of some μm to be produced. Adherence problems between master grating and gel film still have to be solved.

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