UV-curable glassy material for the manufacture of bulk and nano-structured elements

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An ultra violet (UV)-cured glassy material with less than 30 wt% organic residues was fabricated by the fast sol-gel method. The material presents high thermal stability, good optical quality and high adhesive strength. It is suitable for optical bonding and for manufacture of optical elements and micro-structured optical devices. Either soft-lithography or photo-lithography may be used for manufacture of the devices with either, thermal-curing (few hours) or UV-curing (few seconds). In this work we present the technology to fabricate optical elements at scales spanning the sub-micron to centimeter range. This technology enables mass-production of optical elements at low cost. [DOI: http://dx.doi.org/10.2971/jeos.2012.12002]

Keywords: UV-curing, Optical bonding, sol-gel, soft-lithography, photo-lithography, stability

1 INTRODUCTION

Over the past decade, soft-lithography techniques, such as nano-imprinting lithography [1]-[4] and nano-indentation lithography [5] became well accepted methods for fabrication of nano-devices such as solar filters [1], nano-gratings [2, 5], quantum elements [3] and high order symmetry devices [4]. However, these techniques are complicated and expensive.

A less expensive approach relies on fabrication of an inverse replica from a "master" mold or mask, and the subsequent manufacture of the final product by solidifying a liquid precursor against the inverse replica [6]. This method using, elastomeric stamp such as polydimethylsiloxane (PDMS) has been implemented for repeatable production of nanostructures with sub 10 nm features [7]. The solidification of a liquid photo-resists precursor can be achieved by thermal or UV-curing.

However, the current UV-curable photo-resists are based upon polymers with organic polymerizable groups such as epoxy or acrylic. These materials contain a high percentage of organic compounds. They are therefore less durable. In contrast, glassy inorganic materials are not suitable for UV-curing. The sol-gel technology opens an opportunity for material engineering of new classes of UV-curable materials with improved optical and mechanical properties.

Sol-gel is a well known method for preparing glassy materials at temperatures below 100 °C [8, 9]. It allows for introduction or encapsulation of a wide range of inorganic and organic additives in the sol-gel matrix as part of the skeleton structure. The possibility of starting from molecular precursors and elementary building blocks permits

tailoring of structures at a molecular level and creating new materials with enhanced performances. Lately, fabrication of high performance optical sensors, waveguides, lasers and nano-structured materials was demonstrated [10]. The sol-gel process allows designing advanced photonic materials by creating hybrid materials which combine both organic and inorganic functionalities. The use of hybrid sol-gel in UV-cured imprinting and photo-lithography techniques has been reported in recent years [11]-[13]. The precursors for fabricating these materials are usually based on organically modified silanes (ORMOSIL) [14]. The commonly used ORMOSILs are from the organically modified ceramics (ORMOCER) class [15]-[19] which are suitable for UV-curing. However, the ORMOCERS are organic-inorganic hybrids with a high content of organic residuals (~70 wt %) and therefore possess properties that are more similar to organic polymers rather than to silica glass. UV-curable materials with higher inorganic content (50 wt %) were recently demonstrated for fabrication of thin films [20]. However, such process induces a 70% weight loss at 400 °C, indicating low thermal stability due to the high organic content of the final product. An additional example of sol-gel technology for creating hybrid materials with high refractive indices is based on acrylic ORMOCERs with an addition of TiO_2 sols [21]. The photo-polymerization process contains precursors such as epoxy-based 3-Glicydyloxypropyl-trimethoxysilane (GPTMS), or acrylic-based 3-Methacryloxypropyl-trimethoxysilane (MAPTMS, see Figure 1). Their properties as function of irradiation time and UV-radiation dose are reported in ref. [22].

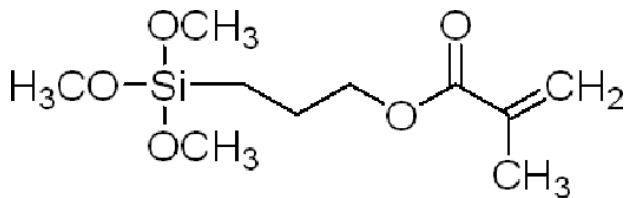We have recently developed a new class of sol-gel materials

FIG. 1 Hybrid sol-gel monomer with one acrylic organic polymerizable tail group, 3-methacryloxypropyl-trimethoxysilane (MAPTMS).

which are a combination of silica alkoxides with organically modified alkoxides and can possess therefore optical and mechanical properties that may vary between silicone rubbers to silica glass [23]. These materials are prepared by the fast sol-gel (FSG) process which leads to solidification without shrinkage or formation of cracks [24]. Such materials with organic residues of less than 30% [25] present high thermal stability, high optical quality and high adhesive strength and may be also used as optical adhesives [26]. The FSG material was demonstrated to have only 4% weight loss at 400 ° C, due to continued inorganic cross-linking [26].

In the current work we present the development of a UV-curable inorganic-organic hybrid resin that enables, upon curing, the formation of a shrink- and crack-free glass-like product containing less than 4 wt% volatiles and less than 30 wt% organic residues. Here we show that the addition of a small amount of organic polymerizable tail groups will cause a significant acceleration in the polymerization rate of the inorganic part, leading to solidification of the entire matrix within a few seconds. The final product prepared in this way presents an excellent transparency in the visible region, an adhesive strength of about 10 MPa, and high thermal stability.

2 EXPERIMENTAL

A detailed description of the fast sol-gel method can be found in ref [24]. Briefly, sol-gel precursors (alkoxides and organically modified alkoxides) are mixed and undergo hydrolysis and condensation. The fast sol-gel reaction is performed at a temperature of about $100^{o}C$ under time-varying pressure conditions (from several atmospheres to vacuum). In this way a viscous sol-gel resin is quickly produced which, after a fast and simple curing process, leads to the final glass-like product. However, for optical bonding applications a long shelf-life is required. By diluting the viscous sol-gel resin with an appropriate solvent shortly after preparation, the diluted material can be kept for several months as a solution. Before use, the diluents can be removed by moderate heating or evaporation.

In order to transform this sol-gel, to an UV-curable polymer, a small amount of organic polymerizable tail with an acrylic bond was added by incorporating a 3-methacryloxypropyl-trimethoxysilane (MAPTMS, a precursor with one organic and three inorganic polymerizable tails, see Figure 1). In this case, the precursor's molar ratio (TMOS:MTMS:MAPTMS) was 1:5.6:0.4. A small amount of a photo-initiator, Irgacure 184, (1 wt %) was also added to the diluted solution of the sol-gel resin.

We have fabricated bulk and nano-structured elements by the reverse replica method: an elastomeric (polydimethylslicone - PDMS) negative master stamp was used to imprint upon a FSG substrate the required pattern. The imprint process involved pouring a viscous FSG resin on a flat substrate (such as silicon wafer), press the stamp and cure the resin (either by UV or thermally). We have used as the reverse-replica stamp elastomeric stamps with patterned relief structures on their surface to generate patterns and structures with feature sizes ranging from a few centimeters down to 300 nm. As elastomeric stamps we used polydimethylslicone (PDMS), a common silicone rubber. For patterned relief, coins were used for demonstrating macro structures, while for the smaller scales micron-scale photo-resist molds were prepared by photo-lithography in a mask-aligner using metal masks. As example, we fabricated a stripe pattern structure on a thin FSG film on silicon substrate [26]. For sub-micron molds we used patterned gold mold prepared by focused ion beam (FIB) or electron beam lithography (EBL). The curing of the sol-gel replicas was done either thermally in an oven at 65 ° C for 12 hours or by UV-illumination for a few seconds (10-30 sec) with a UV Blue Wave 200 (DYMAX) lamp (40 W/cm^2 at 280-450 nm and 7 W/cm^2 at 280-320 nm overlapping the absorption peak of our photo-initiator). In the case of direct photo-lithography, a patterned metal mask was used and the sol-gel was applied as a negative photo-resist using a mask-aligner.

We applied the UV-curing process both on thin film and bulks samples. Generally, the thickness of the thin layer was typically 5 μm and of the bulk samples 2 mm. However, in this FSG process layer thickness can vary from 10 nm up to several mm by controlling coating or molding technique. In both cases, 10 second UV-curing process was enough to achieve solidification.

The UV-curing process was also tested for bonding applications (replacing the thermal curing in the bonding procedure reported in reference [26]). Laser damage threshold was measured on FSG disc sample using a 532 nm Nd:YAG laser (Surelite, Continuum) with 7 ns pulses focused to 15 μm diameter as irradiation source.

3 RESULTS

The fast sol-gel (FSG) process is distinguished by the short time required to achieve a solid monolith based on thermal or UV-curable material with low organic content. The resulting material possesses the following properties: free of cracks and shrinkage, ability to control its refractive index, high thermal stability, high laser damage threshold: 5 KW/cm^2 (CW), 2.5 GW/cm^2 (pulse), strong optical bonding (above 10 MPa), and low optical loss (less than 0.01 dB/cm in the visible range). A summary of these properties is presented in Table 1 below [23]-[26].

The improved thermal and irradiation stability properties of these complex materials can be attributed to the encapsulation of the organic part inside the silica skeleton matrix [23]. Since the organic content in these materials is low (below 30%) we can assume that the organic tails are not fully intercon-

Comments/ Ref	Fast Sol-Gel	Property
Optical loss	$<\ 10^{-2}$ dB/cm in the range $400 - 1100$ nm	10^{-3} dB/cm (at 850nm) [24]
Thermal stability	$>\ 300^oC$	4% weight loss at $400\,^{\circ}$C [26]
Laser damage threshold	CW laser: 5 KW/cm^2, Pulse laser: 6 GW/cm^2	[24]
Refractive index (589 nm)	Can be controlled in the range: $1.4 - 1.5$	[23]
Hardness [MPa]	Can be controlled in the range: $5 - 10,000$	[23]
Tensile strength [MPa]	$>\ 10$ for bonding fused silica to fused silica	[26]
Thermal expansion [1/ ˚ C]	Can be controlled in the range: 50-300 x 10^{-6}	[23]
dn/dT [1/ ˚ C]	Can be controlled in the range: - (100-400) x 10^{-6}	[23]

TABLE 1 Fast Sol-gel (FSG) material properties.

FIG. 2a Replica (left) of metal coin (right) with UV-cured fast sol-gel material manufactured by soft lithography with UV-curing process.

FIG. 2b The sol-gel coin replica doped with fluorescent dye cured in 10 second UV-curing process.

nected, but insulated in pores at the silica matrix, and therefore, shielded from the outside environment. However, we suggest that the initiation of the polymerization of the acrylic group using the UV-curing process leads to cross-linking between close acrylic groups. This situation brings the silica groups closer to each other and therefore accelerates the silica polymerization.

Fabrication of optical elements in the cm-scale was demonstrated by replication of coins used as mold (as shown in Figure 2(a)). An example of encapsulation of an additive (a fluorescent dye, Rhodamine B) in the sol-gel matrix (2 mm thickness) is shown in Figure 2(b). The length of the UV-curing process in this case was 10 seconds only.

The fabrication process of the micron-scale elements consisted of replicating the gold mold in PDMS and subsequently imprinting the PDMS replica on a thin layer (typically 5 μm) of fast Sol-gel coating on a silicon wafer. After $\sim$ 10 sec UV-illumination a robust replica of the original pattern was obtained (see optical microscope photographs in Figure 3).

A similar method was used to demonstrate the low-cost production capability of structured materials in the sub-micron range. A 300 x 300 nm replicated array pattern on a 10 x 10 μm wafer is shown in Figure 4 (optical microscope image) and Figure 5 (SEM image). In this case, the sol-gel was thermally-cured at 65 ˚ C overnight. The structure from the gold master mold was faithfully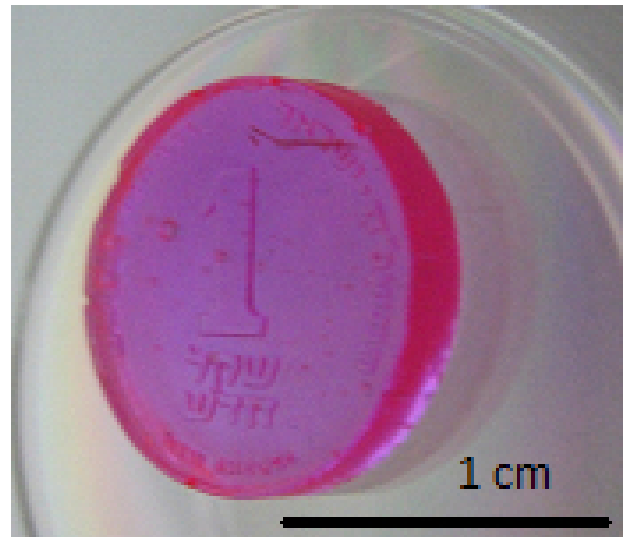 replicated into the sol-gel, included small structural defects such as scratches on the gold master surface (Figure 5) or damage in the array structure (Figure 4).

In addition we developed a process for bonding of glass elements to semiconductor wafers using a UV-curable sol-gel adhesive, requiring only a few seconds (10-30 sec) of UV-illumination. Typical layer thickness was 5 μm. Such bonding was stable under thermal cycling in the range -40 ˚ C up to 120 ˚ C (no reduction in transparency or adhesive strength) [26].

4 CONCLUSION

We have fabricated bulk elements and sub-micron-scale structures using soft-lithography with fast sol-gel (FSG) UV-curable materials. We demonstrated that acceleration of the polymerization rate of the inorganic part can be achieved by addition of a small amount of organic polymerizable tail groups (acrylic) and a photo-initiator. The UV-curing process results in solidification of the entire matrix within a few seconds. We suggest that the initiation of the polymerization of the acrylic group leads to cross-linking between close acrylic groups. This situation brings the silica groups closer to each other and accelerates the silica polymerization.

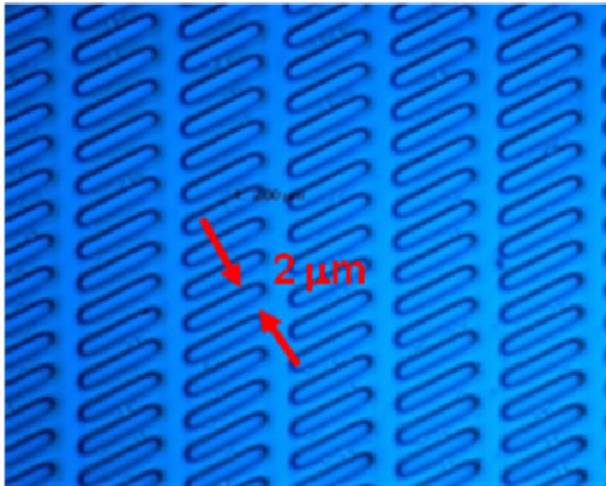The final product prepared in this way posses improved opto-

FIG. 3a Structured devices made with UV-cured fast sol-gel material manufactured by soft lithography. (a) Oval patterned replica and (b) optical circuit replica, photographs taken by optical microscope (Leica).
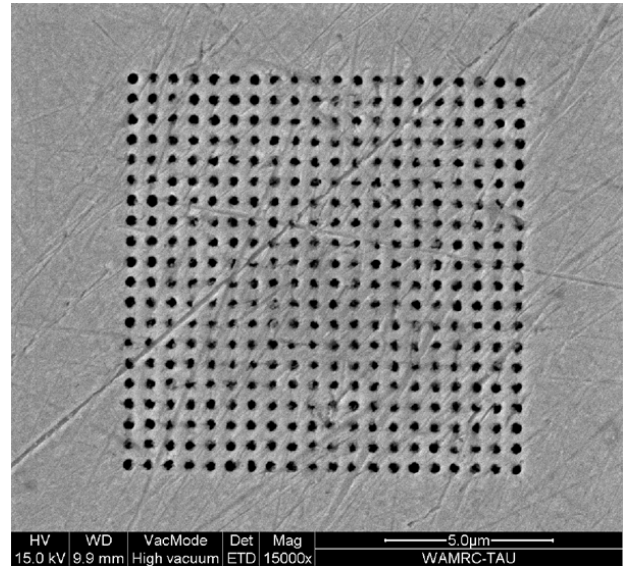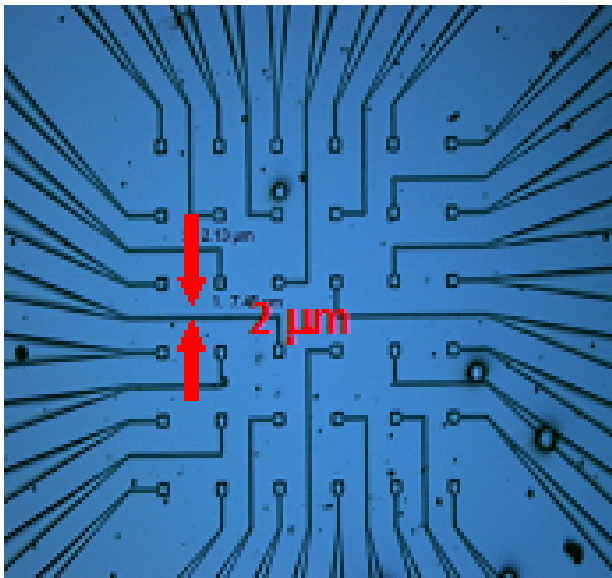

FIG. 3b Structured devices made with UV-cured fast sol-gel material manufactured by soft lithography. (a) Oval patterned replica and (b) optical circuit replica, photographs taken by optical microscope (Leica).
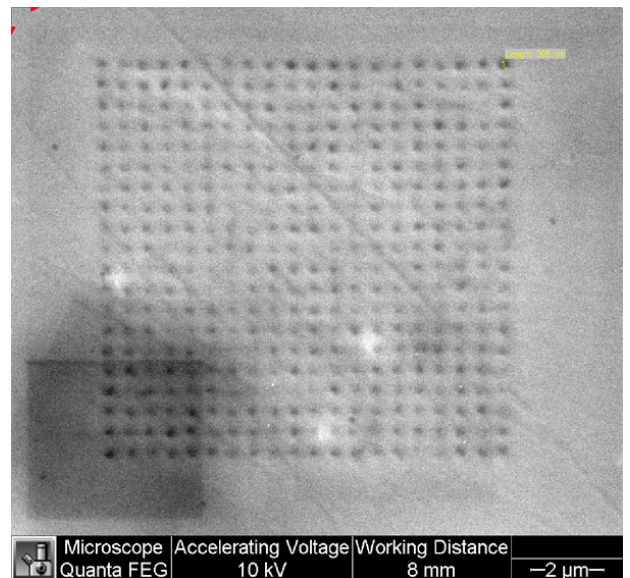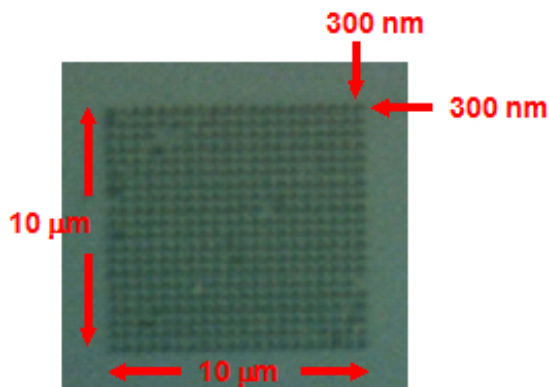

FIG. 4 Nano-scale sol-gel structured array replica prepared by soft-lithography. The master mold consisted of a patterned gold mask, while PDMS was used as an elastomeric stamp. In this case the sol-gel was thermally-cured. Photograph was taken by optical microscope.

FIG. 5a Gold master mold prepared using Focus Ion beam Lithography.

FIG. 5b Sol-gel replica prepared using soft-lithography through a mold of reverse replica.

mechanical properties, presents an excellent transparency in the visible region, an adhesive strength of about 10 MPa, and high thermal stability. We attribute the improved properties to a lower content of the organic part which is shielded from the outside environment by the silica skeleton.

The Fast Sol Gel process is well suited for fabrication of stable and robust UV-curable materials allowing for low cost mass-production of photonic devices and UV curable optical adhesives.

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