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Soft-mould imprinting of chalcogenide glasses

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Nanoimprint lithography, by using a polymeric mould (stamp) such as PDMS (polydimethylsiloxane), is well-established technology for surface replication of micro- and nanometre-sized features into functional materials including low-softening temperature (T_s) thin-films and bulk chalcogenide glasses. Here, we discuss specific conditions of imprinting As_3S_7 chalcogenide bulk glass (T_s ~500 K) by using the soft PDMS mould obtained from a silicon master mould. Imprinting of micrometre and sub-micrometre size patterns (0.5, 1 and 2 μm in width), namely grooves/lands, holes and pillars arrays, is demonstrated.

So far, several studies have been published on soft-mould [1] patterning applied specifically to chalcogenide thin films [2, 3]. These studies focused on fabrication of devices exploiting chalcogenide film/substrate optical contrast for channel and planar waveguides. In contrast to thin-film technology, the present work is on imprinting of chalcogenide bulk glasses [4, 5]. The bulk form has several advantages for practical use over the thin films of corresponding composition: a) reproducible bulk samples can be obtained easily, therefore there is no thin-film deposition required; b) physico-chemical properties of thin films are very dependent on deposition technique used [6]; c) bulk glasses are more mechanically and thermally stable; d) bulk glass serves as its own substrate, eliminating the film-substrate interface (adhesion and cracking issues) and e) thin films deteriorate faster under external stimuli like laser pulses, reaction with water vapours, mutual aging etc. [7].

The patterns, imprinted into the chalcogenide As_3S_7 glass, were achieved simply by heating the glass sample, which had been polished to optical quality ($\sigma_{RMS} \approx 1$ mn), laid on the surface of the PDMS mould. The PDMS mould was fabricated by NIL Technology ApS, Kongens Lyngby, Denmark, using a silicon master mould.

The imprinting pressure arose solely from the sample weight (~1 g) acting on the contact area ~1 cm^2. The imprinting temperature control had three stages: (i) heating from room temperature up to the imprinting temperature, T_{imp} = 498 K with heating rate 10 K min^{-1}; (ii) an isothermal hold for 40 minutes, and (iii) cooling down at rate 5 K min^{-1} to room temperature (Fig. 1). The low-load soft-mould imprinting of bulk glasses has some key advantages and specific limitations in comparison with commonly used hot-embossing of chalcogenide thin films [8]. The embossing temperature is typically at temperatures 10–30 K above the glass-transition temperature (T_g) for thin films corresponding to supercooled-liquid shear viscosity, η ~10^9 Pa s. This corresponds to T = 448 K for the As_3S_7 glass. The softening of the film, at these lower temperatures, is then only moderate and larger imprinting loads, typically in the range of 0.1–0.2 MPa for chalcogenide glasses, have to be used. The substrate material must have the T_g greater than that of the thin film to withstand the imprinting pressure, avoiding plastic deformation, and the substrate should have a thermal expansion coefficient similar to that of the film to avoid film cracking and delamination. This is not a problem for direct imprinting of bulk glasses, which are effectively their own substrates.

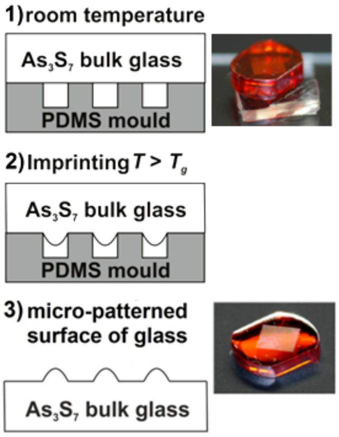

Figure 1. A schematic of A_3S_7 glass imprinting technology. Optical micrographs show the glass/PDMS stamp at room temperature and corresponding imprinted pattern. Sample dimensions are ~1×1 cm.

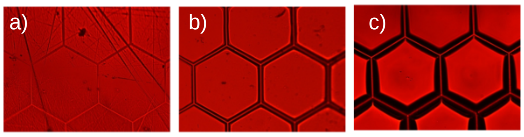

Figure 2. Demonstration of T_{imp} influence on PDMS pattern replication into the chalcogenide glass. The T_{imp} corresponds to a) 493 K, b) 498 K and c) 503 K.

The importance of an accurate control of soft-stamp imprinting temperature is demonstrated in Figure 2 using array of hexagons as an example. All patterns were imprinted using the same procedure with the only difference being the T_{imp} = 493, 498 and 503 K, respectively. In case of the T_{imp} = 493 K (Fig. 2a), the imprinting temperature was not high enough to replicate the whole depth of the PDMS mould into the glass surface. The imprinting was optimized at holding temperature T_{imp} = 498 K to achieve the best replication in all three dimensions (Fig. 2b). On the other hand, further 5 K increase in the imprinting temperature (Fig. 2c) caused rounding and broadening of the channels' edges, which corresponds to the softening temperature of the glass resulting in significantly increased liquid flow. The optimized T_{imp} = 498 K is just 5 K below the T_s of As_3S_7 glass, and 80 K above T_g, which corresponds to $\eta \approx 10^6$ Pa s. Such high temperatures are typical for chalcogenide glass fibre-drawing processes, where viscosities in the range 10^6–10^8 Pa s are representative for glass-rod necking and starting the fibre-drawing of glasses such as As_2S_3 or As_2Se_3 [9]. The ease of shaping makes these chalcogenide glasses good candidates for nanoimprint lithography. In both, nano-imprinting and fibre-drawing techniques, the glass shaping is an equilibrium process, which strongly depends on the temperature dependence of the supercooled liquid viscosity. The viscosity of the glass has to be accurately controlled by keeping the temperature within few units or tens of degrees limits, to achieve the best flow conditions. This optimization is required for each glass depending on its composition. For proper removing of the PDMS, the chalcogenide glass/stamp has to be cooled down to the room temperature. While at high temperatures there are strong adhesion forces between the PDMS and the chalcogenide glass, at low temperatures, the adhesion is very weak and PDMS can easily be removed without any damage to either the glass or the PDMS. The same PDMS stamp can be re-used several times.

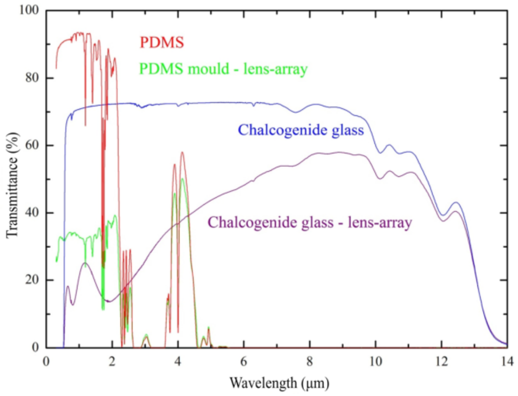

Figure 3. Comparisons of Mid-IR transmittances do not show any noticeable contamination of the imprinted sample either due to oxidation nor by the PDMS residua.

Because the imprinting was done under normal atmosphere any influence of potential contamination from the PDMS mould, and its residua, and the glass oxidation or reaction with water vapours has been examined. Infrared transmittance data (Fig. 3), measured on the lens array, have not shown any significant contribution of any of the either above mentioned effects.

The final imprints, achieved via the method described above, are shown in Fig. 4. Features 0.5, 1 and 2 μm in width were successfully and reproducibly replicated into the As_3S_7 bulk glass. In case of 0.5 μm only pillars could be reproduced. The grooves/lands and holes array could not be imprinted because a high quality PDMS replica could not be obtained from the silicon master mould. The typical surface roughness of the imprints in the As_3S_7 glass is $\sigma_{RMS} \approx 3$ nm. The main imperfections originate from the PDMS stamp itself. It has been demonstrated that a sub-micrometre grating with periodicity 625 nm and amplitude 45 nm can be imprinted in chalcogenide glass over large area [5].

Soft imprint lithography using the PDMS mould has been shown as an effective and straightforward method for micrometre and sub-micrometre patterning of the surfaces of bulk chalcogenide glasses. Using commercially available nano-imprinters soft imprinting of bulk chalcogenide glasses shows great promise for reproducible fabrication of optical and photonic devices over large-surface areas. The high refractive index of chalcogenide glasses could be exploited in the design and fabrication of diffractive optical elements for the infrared region such as relief diffraction gratings for filtering light of selected spectral range or patterning of anti-reflection surfaces as lens arrays with optical properties tuned at any particular wavelength.

Further refinement of the patterns down to nanometre scale is expected to be useful in other applications; examples include sensors operating in the visible and infrared spectral range, optical elements based on an optical non-linearity, surface-enhanced effects, evanescent light generation or plasmonic edge tuning.

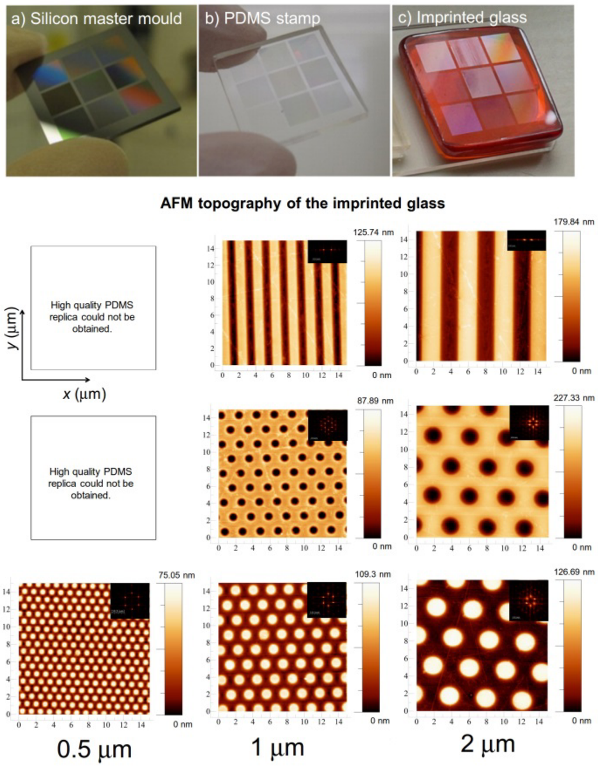

Figure 4. Optical micrographs showing: a) the starting silicon master mould with 3×3 array; b) the fabricated PDMS stamp with inversed pattern profile to the master mould, and c) the imprinted As_3S_7 chalcogenide glass. Bottom panels show topography of the imprinted chalcogenide glass measured by atomic-force microscopy (15×15 μm scan size) and processed using WSxM software [10]. The insert figures represent a fast-Fourier transformation of the topography images, where the scale bar corresponds to the individual pattern widths 0.5, 1 and 2 μm, respectively.

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