Sub-micrometer soft lithography of a bulk chalcogenide glass

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Abstract: We demonstrate, for the first time, time- and cost-effective replication of sub-micrometer features from a soft PDMS mold onto a bulk chalcogenide glass over a large surface area. A periodic array of submicrometer lines (diffraction grating) with period 625 nm, amplitude 45 nm and surface roughness 3 nm was imprinted onto the surface of the chalcogenide AsSe2 bulk glass at temperature 225°C, i.e. 5°C below the softening point of the glass. Sub-micrometer soft lithography into chalcogenide bulk glasses shows good reliability, reproducibility and promise for feasible fabrication of various dispersive optical elements, antireflection surfaces, 2D photonic structures and nano-structured surfaces for enhanced photonic properties and chemical sensing.

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1. Introduction

Nano-imprint lithography (NIL) [1,2] is a highly scalable (lateral resolution finer than 10 nm has been demonstrated [3]), effective, straightforward and low-cost parallel processing technique, which has been extensively used for surface patterning of inorganic and organic solids [4,5]. NIL can be used with hard (quartz, silicon, metal, or tungsten carbide, etc.) molds, with which imprinting has been demonstrated for optical waveguides (4.5−6 μm wide and 2 μm high) into As_2Se_3 film by using Si mold during hot embossing [6], sub-micrometer nano-cone arrays into $Ge_{15}As_{15}Se_{17}Te_{53}$ bulk glass by using Si mold [7], sub-micrometerperiod wire-grid polarizer into Sb-Ge-Sn-S bulk glass by using SiC mold [8], micrometer-size anti-reflection surfaces at the ends of infra-red (IR) As_2S_3 chalcogenide glass (ChG) fibers by using Ni mold [9], and sub-micrometer diffraction grating in $Ge_{20}As_{20}Se_{14}Te_{46}$ bulk glasses by using Si, SiO_2 and Ni molds [10].

Recently NIL, using molds of soft polymers, like polydimethylsiloxane (PDMS), has been used to prepare optical waveguides (2−4 μm wide and 1 μm high) in $As_{24}S_{38}Se_{38}$ thin films with significantly reduced attenuation losses ~0.26 dB/cm at 1550 nm [11]. Similarly PDMS imprinting of micrometer-size waveguides into thermally evaporated thin films As_2S_3 has been demonstrated [12,13]. Tsay et al. [14] used solution of As_2S_3 glass dissolved in propylamine, which was forced into micro-channels of PDMS mold and after baking-off and removing PDMS 'mold' micrometer-size single-mode waveguides (2.5 μm wide and 4.5 μm high) have been prepared. The main advantages of PDMS as a mold material are its good compliance and easy peel-off from ChG after cooling, i.e. at room temperature (RT). NIL is a competing technology to traditional optical lithographic techniques [15], direct laser writing (DLW) [16], holography [17], and focused ion beam (FIB)

milling [18], all of which are costly, time-consuming and complex. It is the DLW which has been gaining lots of interest especially for its versatility in patterned shapes and variety of materials being used [19]. Soft lithography in comparison with direct laser machining into the chalcogenide bulk glasses, for example as in [16], brings several advantages especially in reduced surface roughness of the patterns, low-cost facility contrary to fs-lasers, capabilities of extremely fast large-area and repeatable mass-production due to its ability of multiple replications of cheap PDMS softmold from costly master-mold. Also, rather often neglected, the ChGs, in form of thin films and bulks, suffer from burning when exposed to fs-lasers and the composition is altered. On the other hand the PDMS lithography is currently limited to 'soft' ChGs due to the thermal stability of the soft stamp itself.

ChGs [20,21] are transparent up to far-IR wavelengths (~20 μm); they have high optical nonlinearity and can easily be doped with rare-earth ions exhibiting, for example, strong photoluminescence. All these factors make ChG materials of choice for IR optical components (lenses, prisms and filters), functional devices for non-linear optics (fibers or waveguides [22,23]), and chemical sensors [24,25], which all have been mainly fabricated using traditional techniques. Recently, growing efforts have been devoted to planar devices and surface-enhanced effects in bulk and thin-film ChGs. FIB nanostructured ChG surfaces (an array of ~200 nm diameter holes milled in 150 nm thin films) with enhanced visible-light photon up-conversion were reported in Er^{3+}-doped Ga-La-S-O films [26]. Su et al. [25] used a holographic technique for nano-patterning of an As_2S_3 film (array of near semicircular dots ~450 nm in diameter and 70 nm in height and intervening holes), followed by deposition of a gold layer to obtain SERS (surface-enhanced Raman scattering) substrates. Optical waveguides (2 μm wide and 0.87 μm high) were produced in As-S thin films [22] by selective plasma etching showing wide super-continuum generation upon pumping with fs-laser pulses. Nonlinear waveguides (3 μm wide and 2 μm high) were produced also as parts of photonic circuits in As-S-Se films [27].

In this paper, we describe first-time **sub-micrometer**, in scale both laterally and vertically, **imprinting** of a periodic diffraction grating onto the surface of the **chalcogenide bulk** glass $AsSe_2$ **using a soft PDMS mold**. We do not intend to fabricate accurately defined diffractive gratings, but rather to demonstrate and explore the capabilities of soft imprinting in chalcogenide glasses at sub-micrometer level. This paper follows our previous report on softmold micrometer-scale patterning of the chalcogenide bulk glass As_3S_7 [28]. The feasibility and reliability of sub-micrometer soft lithography on bulk ChGs is investigated, a motivation being that there are still challenges in obtaining functional chalcogenide nanostructured photonics, photon conversion and sensor-based devices. Bulk glasses have benefits in easy fabrication and good chemical, thermal, mechanical and high-power laser-irradiation stability, in contrast to thin films.

2. Experimental

A commercial silicon master mold with a grating motif, fabricated on an n-type silicon wafer by standard photolithography, was available from Lightsmyths Co. Ltd., USA. The PDMS replica was made from an elastomer kit (Sylgard 184, Dow Corning) using a 10:1 mixture of a base oligomer to curing agent. The mixture was poured over the silicon master mold and degassed in a vacuum chamber for 30 minutes. After curing at RT for 12 hours and at 60°C for more than 3 hours, the PDMS replica (resulting thickness ~4 mm) was peeled off the silicon master mold. The PDMS mold is stable at least up to 250°C. Chalcogenide $AsSe_2$ bulk glass (glass-transition temperature T_g = 162°C and softening temperature T_s = 230°C measured by thermo-mechanical analysis) was prepared in the form of a rod by direct synthesis from 5N pure elements using standard melt-quenching. The $AsSe_2$ rod (slowly annealed at T_g−10°C for 4 hours) was cut into plane-parallel slices and polished to optical quality (roughness, σrms ≈1 nm).

Imprinting of the chalcogenide bulk glass was done by heating the glass disk laid on the surface of the PDMS mold without using any nano-imprint facility, accurate alignment or pressure control. The imprinting pressure arises solely from the sample weight (~1 g, thickness ~2 mm) acting on the contact area (~1 cm2). The heat treatment has three stages: (i) heating from room temperature (RT) up to the imprinting temperature T_{imp} = 225°C in 30 minutes, (ii) an isothermal hold for 30 minutes, and (iii) cooling down to RT in 90 minutes and peeling off the PDMS mold at RT (Fig. 1). The condition T_{imp} = 225°C was found to be the best for accurate pattern reproduction from the PDMS mold to the $AsSe_2$ glass.

The imprinted surface topography was measured using atomic force microscopy (AFM): Veeco 3100, in tapping mode, using an 8 nm radius Si tip, software WSxM 5.0 develop 5.3 [29]. The optical transmittance (Jasco V-570) was measured for the plain $AsSe_2$ bulk glass disk, for a disk imprinted at T_{imp} = 225°C, and for a disk annealed at T = 225°C to search for any influence of the imprinting (contact with PDMS mold resulting in

potential contamination), and temperature treatment on the overall transparency of the sample. The first-order diffracted TM- and TE-polarizations were recorded using a spectroscopic VASE ellipsometer (from J. A. Woollam Co. Inc., Lincoln NE, USA) operating in reflection mode, where the beam-to-sample angle was set to normal (halogen bulb white source), and the detector-sample angle was moved in steps of 5° from normal to 40°.

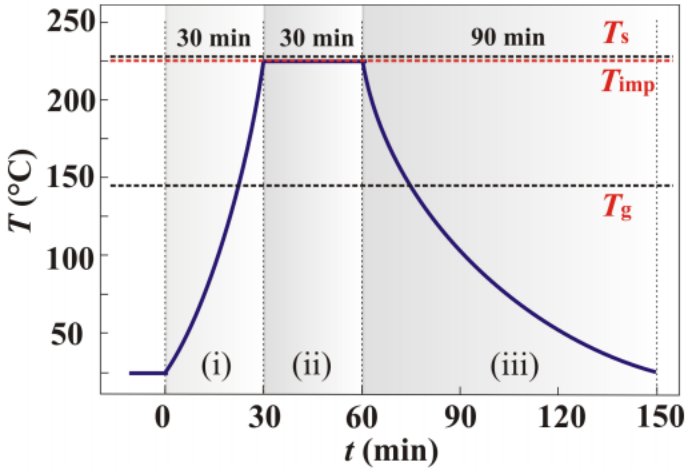

Fig. 1. Temperature history of the $AsSe_2$ glass, during three-step low-load soft imprinting (see text for details).

3. Results and discussion

The low-load soft-mold imprinting of sub-micrometer features into the chalcogenide bulk glass has some key differences and specific limitations in comparison with hot-embossing of chalcogenide thin films performed on commercial or home-made nano-imprinters mainly using hard molds, e.g. such as in [6] describing imprinting of optical waveguide into As-Se film. The embossing temperature is typically at temperatures 10−30°C above T_g for thin films, at a supercooled-liquid viscosity (η) of ~10^9 Pa.s (Fig. 2), which corresponds to T = 175°C for $AsSe_2$ glass. The softening of the film at these temperatures is then only moderate and larger imprinting loads, typically 0.1−0.2 MPa, have to be used. The substrate material must have a T_g greater than that of the thin film to withstand the imprinting pressure (i.e. to avoid viscous flow), and should have a thermal expansion coefficient similar to that of the film to avoid film cracking and delamination, such as are seen, for example, for a low-temperature chalcogenide film of As-Se on a high-temperature Ge-As-Se bulk substrate [6]. This is not a problem for bulk glasses, which are in effect their own substrates. In both techniques, embossing and imprinting, the films and bulk samples are, however, very sensitive to wedge-shaped defects caused by misalignment arising from non-parallel polishing (in the case of a bulk glass), or from inaccurate control of the deposition process (in the case of a thin film). With soft lithography, the bulk glass can easily flow and fill in the patterns of the PDMS mold at very low imprinting pressures because of the high T_{imp} which is close to T_s. Nanoimprint lithography of chalcogenide glasses and films with a soft PDMS mold has the advantage that, at any temperature during the soft-imprinting process, the mold is flexible enough to relieve stresses occurring during cooling near T_g.

Temperature control is important both for imprinting bulk glasses and for embossing thin films. In our case the T_{imp} = 225°C is only 5°C below Ts and corresponds to η ≈10^6 Pa.s [30]. Such high temperatures are typical of a ChG fiber-drawing process, where viscosities in range 10^6 −10^8 Pa.s are typical for glass-rod necking and starting the fiber-drawing of glasses such as As_2S_3 or As_2Se_3 [31]. The ease of shaping makes these chalcogenide glasses compositions good candidates for NIL. In both nano-imprinting and fiber-drawing, the glass shaping is an equilibrium process and strongly depends on the temperature dependence of the supercooledliquid viscosity. The viscosity of the glass has to be precisely controlled, by holding the temperature within a few degrees, to achieve the best flow conditions and this requires optimization for each glass depending on its composition. Typical good glass forming ChGs (As-S, As-Se), chosen for soft-mold imprinting and fiber-drawing, have supercooled liquids of strong-to-medium fragility [32].

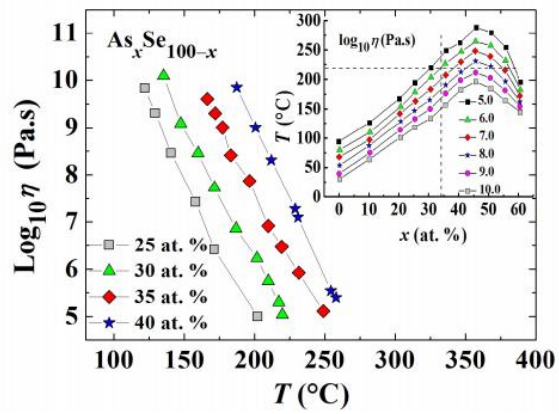

Fig. 2. The dependence of As_xSe_{100-x} supercooled liquid shear viscosity on temperature. The lines are guides for the eye only. The dashed lines, in the inset figure, correspond to the composition $AsSe_2$. The data are from [30].

To demonstrate the potential of soft lithography for sub-micrometer patterning on chalcogenide bulk glasses, we imprinted a diffraction grating with period d ≈625 nm, depth (amplitude) h ≈45 nm (Fig. 3) and surface roughness σ_{rms} ≈3 nm. The imprinted grating dimensions are similar to gold-coated diffraction gratings of similar topology used, for example, in surface-plasmon generation and SERS sensing [33]. AFM topography shows that the average grating amplitude is the same for the PDMS mold and the patterned glass. In each case the grating profiles are nearly sinusoidal with the minima and maxima consistently distributed across grooves and lands, respectively. The main imperfections originate from Sylgar 184 elastomer kit itself, which is primarily used for micrometer rather than nanometer patterning. The defectiveness of the PDMS mold is apparent in the unevenness of the lands (Fig. 3(a)). These were then imprinted into the bulk glass and appear in the grooves of the replica (Fig. 3(b)), where grooves and lands are more even than in PDMS mold caused likely due to 'limited' viscous flow of the glass at low loads, which does not allow copying all the stamp imperfections at nano-scale size. Also a surface energy at the imprinted scale can play important role but its effect has not been studied yet in detail. We may expect improvement of soft nanometer-scale lithography on chalcogenide glasses with progress in the development of polymer molds from nano-PDMS elastomer kits as shown, e.g. in [34].

In principle, nano-imprint lithography has the potential to make gratings with nonsinusoidal profiles [8] when the relief fabricated into the master mold is designed appropriately. This opens up possibilities for obtaining diffraction gratings with blazed or trapezoidal shapes similar to those achievable by the classical rolling technique or by anisotropic etching. Gratings of non-sinusoidal profile are difficult to obtain with photolithography or holography techniques due to the light propagation limits.

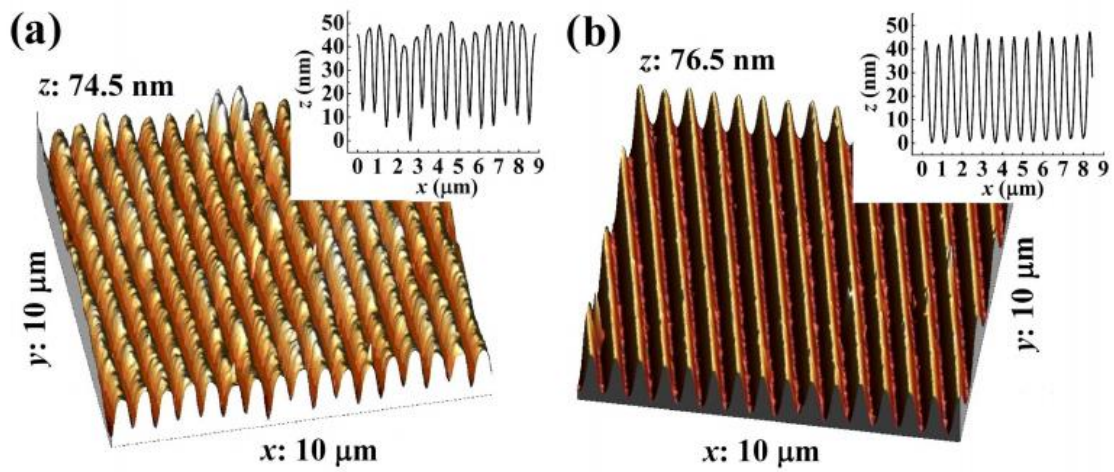

Fig. 3. AFM topography images showing (a) the PDMS mold and (b) the imprinted $AsSe_2$ glass. The inset figures show the surface profiles.

Figure 4 shows the transparency window of chalcogenide $AsSe_2$ glass disks: (a) a polished disk, plain on both sides (dotted line), (b) the same disk annealed at T = 225°C (dashed line), and (c) a similar disk patterned on one side with a PDMS mold at T_{imp} = 225°C (solid line). Comparison of their transmittance spectra reveals absorption bands at 12.6 μm originating from Se-OH bonds and at 15.3 μm attributable to the CO_2 [35] present in the ambient atmosphere in the spectrometer. Absorption at 12.6 μm revealed partial hydrolysis even for the plain $AsSe_2$ glass disk, whose synthesis did not include any additional purification of the raw (5N) elements. This step is necessary for obtaining ChGs with low impurity levels. Weak bands from water absorption are detected near 2.8 and 6.08 μm, and 3.53 and 4.12 μm originating from Se-H bonds. The spectra of the patterned chalcogenide glass disk are not significantly affected by either the imprinting procedure, i.e. thermal treatment and crystallization, nor by the contamination of the glass surface by PDMS mold residues.

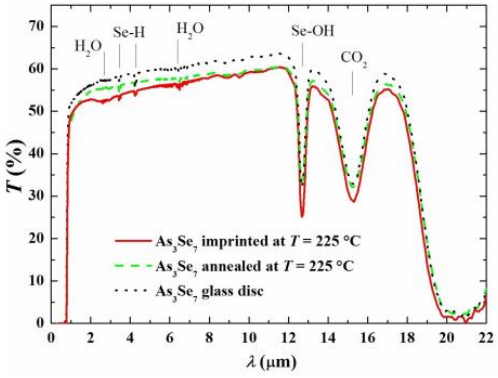

Fig. 4. The transmittance of a plain, as-prepared glass disk, a glass disk annealed at T = 225°C, and a glass disk imprinted at T_{imp} = 225°C. No apparent increase in the level of impurities (change in IR absorption) or glass crystallization (change in transmittance or shift in short wavelength absorption edge) caused by imprinting process were observed. The disks are ~2 mm thick.

The spectral dependence of experimentally obtained first-order diffraction TM- and TEpolarized light intensities is shown in Fig. 5. The diffracted light was measured in the range 300–750 nm for oblique diffracted angles Φ_r = 85–45°. The white light beam was kept at normal incidence to the grating surface. The positions of diffracted peaks (λ_c), calculated using the grating equation and measured (λ_m), are compared in Table 1. The experimental spectra correspond well with the theoretical values. There is a constant offset of 6−8 nm between the calculated and measured positions of diffracted peaks. This is likely due to beamto-sample and sample-to-detector misalignments, where ± 1° of angular shift corresponds to ± 10 nm change in peak position.

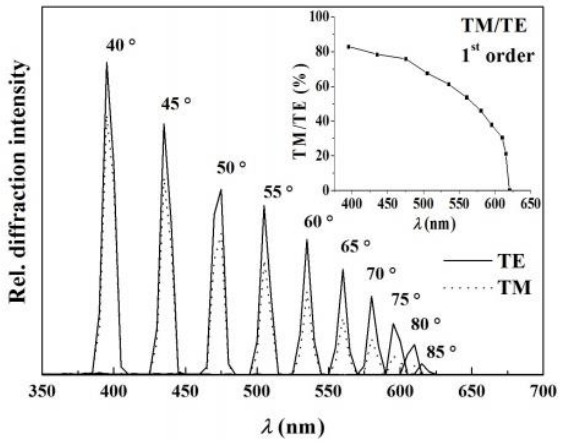

Fig. 5. Comparison of the relative intensities of TM and TE modes measured for first-order diffraction with the beam at normal incidence on the sample.

Table 1. Light dispersion from an imprinted $AsSe_2$ glass grating was calculated for the first-order diffraction and compared with measured data (Fig. 5). The grating period d = 625 nm was taken in the calculation, corresponding to the average value according to AFM. The diffraction angle Φ_r is that between the incident beam and the detector axis.

Φ_r (deg)	λ_c (nm)	λ_m (nm)	$\lambda_m - \lambda_c$
90	625.(0)	–	–
85	622.(6)	616	−6.(6)
80	615.(5)	610	−5.(5)
75	603.(7)	595	−8.(7)
70	587.(3)	580	−7.(3)
65	566.(4)	560	−6.(4)
60	541.(3)	535	−6.(3)
55	511.(9)	505	−6.(9)
50	478.(8)	473	−5.(8)
45	441.(9)	435	−6.(9)
40	401.(7)	395	−6.(7)

4. Conclusions

We have clearly demonstrated that sub-micrometer patterns such as a diffraction grating (amplitude 45 nm and period 625 nm) can be imprinted into a bulk chalcogenide glass by using a PDMS mold. Soft lithography has been shown to be an effective, straightforward method for sub-micrometer patterning of the surfaces of bulk chalcogenide glasses. However, precise control of the replication process, on a nanometer scale both laterally and vertically, has to be realized. Considered for industrial use, the soft imprinting of bulk chalcogenide glasses shows great promise for the reproducible fabrication of optical and photonic devices over large surface areas. The high refractive index of chalcogenide glasses can be exploited in design and fabrication of 2D photonic crystals, optical elements for the infrared region, e.g. relief diffraction gratings and filters with anti-reflection surfaces, or sensor arrays such as for SERS, nanostructured surfaces promoting enhanced photon up- or down-conversions etc.

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