

# Structuring of solution processed and thermally evaporated $\text{As}_{33}\text{S}_{67}$ thin films by soft stamp hot embossing method

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## Abstract

Chalcogenide  $\text{As}_{33}\text{S}_{67}$  vitreous thin films prepared by thermal evaporation and spin-coating method from n-propylamine and n-hexylamine based solutions were structured using hot embossing technique with soft PDMS stamps. The influence of deposition method and conditions as well as thermal history of the samples was studied. Obtained results gave evidence that solution processed thin films can be structured at significantly lower temperatures in comparison with thermally evaporated thin films, even below  $T_g$  of the glass. Theory explaining observed phenomena based on the structural differences of solution processed and thermally evaporated thin films was proposed. Notable decrease in required embossing temperature of solution processed thin films will widen the range of chalcogenide glass compositions that can be structured by soft stamp hot embossing as well as the pool of usable substrates (such as substrates with lower temperature stability).

## 1. Introduction

Chalcogenide glasses are intensively studied materials for their wide transparency in IR region, high values of refractive index and frequent photosensitivity. Chalcogenide glasses, especially in a thin film form, found practical applications as suitable material for optical components (e.g. planar waveguides, lenses or diffractive optical elements) [1]. Thin films can be deposited either by physical vapor deposition techniques (such as thermal evaporation [2], sputtering [3], laser or electron beam ablation [4]) or techniques based on solution deposition (such as spin-coating [5], spiral bar-coating [6], inkjet printing [7] or electrospray [8]). Even though solution based deposition techniques are simpler (thus cheaper), certain disadvantage is residual amount of organic solvents influencing thin films properties. The content of organic residuals can be significantly reduced by proper post-deposition thermal treatment [9, 10] bringing properties of solution processed thin films close to those of thin films prepared by physical vapor depositions [11].

Practical applications of chalcogenide thin films often require structuring of the surface (e.g. fabrication of waveguides, microlenses, etc.). Lithographic techniques (such as photolithography [12], electron beam lithography [13], direct laser writing techniques [14] or hot-embossing [15]) are usually applied. For structuring can be used solution of chalcogenide glass in form of thin liquid films [16] or using capillary force when PDMS mold is filled by solution and after is PDMS mold put on substrate and bake [17].

Hot embossing is well-established, simple and cost-effective technique for preparation of required structures. Properly chosen time, pressure and temperature of the embossing are necessary to acquire high-quality features. In case of chalcogenide glasses both hard stamps [18] as well as soft stamps [15] can be used. While hard stamps are more resilient to higher temperatures, soft stamps are cheaper to replicate thus more appropriate for low cost applications.

In presented paper we report on the influence of the embossing temperature on the depth of the sinusoidal diffraction grating imprinted in thin  $\text{As}_{33}\text{S}_{67}$  chalcogenide films. Structured thin films of the same  $\text{As}_{33}\text{S}_{67}$  composition were prepared by multiple techniques and under different conditions. First set of thin films was prepared by standard vacuum thermal evaporation technique traditionally used in chalcogenide

glass thin film studies. Second set of samples was prepared through solution process by spin-coating method. Two aliphatic amines were used for source bulk glass dissolution – n-propylamine (n-PrNH<sub>2</sub>) containing three carbon atoms in the aliphatic chain and n-hexylamine (n-HexNH<sub>2</sub>) with six carbon atoms. All samples were studied in as prepared form and spin-coated thin films also annealed at 140 °C for one hour in argon filled chamber. Solution processed thin films undergo significant structural changes during annealing at temperature close to the T<sub>g</sub> [10] which in case of As<sub>33</sub>S<sub>67</sub> chalcogenide glass is 145 °C [19].

## 2. Experimental details

The source bulk glass of As<sub>33</sub>S<sub>67</sub> composition was prepared by standard melt quenching method from high purity (5N) elements. The corresponding amounts of elements were weighed into a clean quartz ampoule which was subsequently sealed under vacuum (~ 10<sup>-3</sup> Pa). Glass was melted for 36 hours at 850 °C in rocking tube furnace and consequently quenched in cold water.

Thermally evaporated thin films were prepared from source bulk glass using UP-858 (Tesla) evaporation device. Soda-lime glass slides were used as substrates. Evaporation was performed under the pressure ~10<sup>-3</sup> Pa using evaporation rate 1.8 nm·s<sup>-1</sup> with final thickness 420 nm. Thickness of thin film and evaporation rate were controlled by quartz crystal microbalance method using device STM-2 (Inficon).

Source bulk glass was crushed in agate bowl and dissolved in n-PrNH<sub>2</sub> and n-HexNH<sub>2</sub> at concentrations 0.075 g glass per 1 ml of n-PrNH<sub>2</sub> and 0.1 g glass per 1 ml of n-HexNH<sub>2</sub>. Fully dissolved solutions were clear, without any turbidity or precipitates. Spin-coated thin films were prepared using spin-coater SC110 (Best Tools) at 5000 rpm for n-PrNH<sub>2</sub> based solution and 1700 rpm for n-HexNH<sub>2</sub> based solution on soda-lime glass substrates. Thin films were stabilized immediately after the deposition for 20 minutes at temperatures 35 °C in case of n-PrNH<sub>2</sub> and 115 °C for n-HexNH<sub>2</sub> (hereinafter referred as “as-prepared”). As-prepared films were subsequently annealed at 140 °C for 1 hour in argon filled chamber. Annealing temperature was chosen with respect to the T<sub>g</sub> of bulk glass (T<sub>g</sub> = 145 °C [19]). Based on our previously published study of solution processed As<sub>33</sub>S<sub>67</sub> thin films [20], the glass solutions concentrations and deposition parameters were adjusted to obtain thin films of thickness ~ 410 nm for as-prepared n-PrNH<sub>2</sub> based thin films decreasing to ~ 220 nm after annealing. Thickness of as-prepared n-HexNH<sub>2</sub> thin films was ~ 250 nm, after annealing decreased to ~ 225 nm.

Soft stamps for hot embossing were prepared from elastomer kit QSil216 (ACC silicones) with mixture ratio 10:1 of base oligomer to curing agent. Mixture was stirred for 30 minutes and then poured over the master holographic grating. Poured master with PDMS mixture was degassed in vacuum and then cured in oven for 1 hour at 110 °C. For hard curing was PDMS stamp peeled from the master grating and annealed at 200 °C for 3 hours. Prepared PDMS stamps had 790 ± 10 nm period and 160 ± 3.9 nm depth.

Hot embossing was performed on heating plate HT 02 (HARRY GESTIGKEIT GMBH). Embossing times (5 minutes and 15 minutes) and pressure (182 kPa) were fixed parameters. Temperatures of hot embossing for individual samples were set in 5 °C increments. Depths of imprinted diffraction gratings were measured by atomic force microscope Solver Next (NT-MDT) equipped with silicon tip NSG10 (NT-MDT). Five 5x5 μm areas (corners and center of diffraction grating) were measured. Presented results are mean values of measured data and error bars stand for standard deviation.

## 3. Results and discussion

The dependence of embossed gratings depths on the embossing temperature is provided in Figure 1.

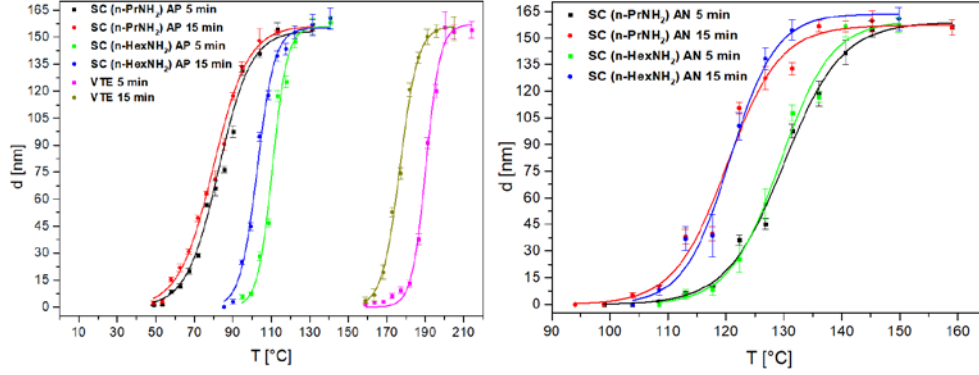


Figure 1: Embossing temperature dependence of the gratings depths for as-prepared (AP) (left) and annealed (AN) (right)  $As_{33}S_{67}$  thin films deposited by vacuum thermal evaporation (VTE) and spin-coating (SC) from n-PrNH<sub>2</sub> and n-HexNH<sub>2</sub> based solutions.

The AFM scans of the diffraction gratings prepared in all studied thin films at the temperature, where the depth of the grating reached the saturation are provided for illustration in Figure 2.

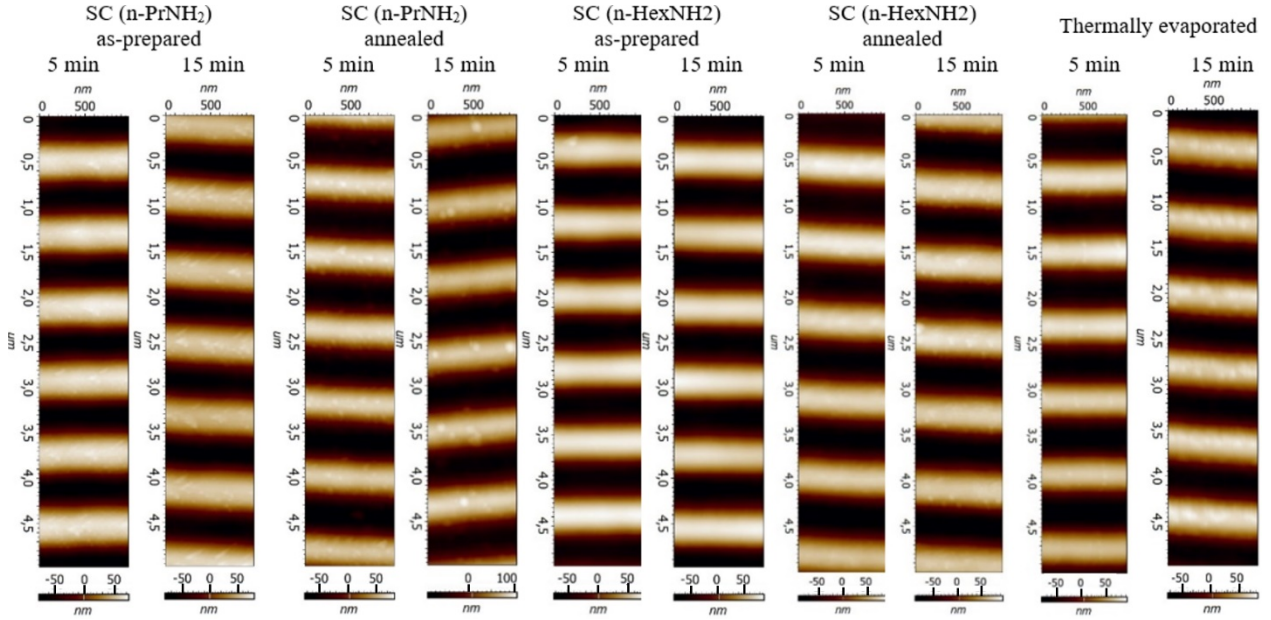


Figure 2: AFM scans of prepared diffraction gratings in all studied thin films.

Obtained data presented in Figure 1 gave evidence that the depth of imprinted gratings is dependent on the embossing temperature in sigmoidal character independent on the method and conditions of the deposition or thermal treatment of prepared thin films. For better description of measured dependences, obtained data were fitted by modified Boltzmann function

$$d = \frac{d_{MAX}}{1 + e^{(T-T_0)/dT}} \quad (1),$$

where  $d$  is the depth of the grating at the embossing temperature  $T$ ,  $d_{MAX}$  is the maximal grating depth (practically limited by the depth of the PDMS stamp) and  $T_0$  is the temperature where the curve reaches inflex point. Fitted curves are also provided in Figure 1 as solid lines. By derivation of equation (1) the slope  $s$  of the curve in the inflex point can be calculated as:

$$s = \frac{d_{MAX}}{4dT} \quad (2).$$

The slope can be interpreted as sensitivity of the material to the embossing temperature in order to be structured under given conditions. Higher values of the slope mean that small changes in the embossing temperature will result in bigger differences of the depth of imprinted structures.

Values of parameters  $d_{MAX}$ ,  $T_0$  and  $s$  obtained by fitting of experimental data with function (1) and (2) are provided in Table 1.

Table 1: Values of  $d_{MAX}$ ,  $T_0$  and  $s$  obtained from equation (1) and (2) for gratings prepared in spin-coated (SC) and thermally evaporated thin films at 5 and 15 minutes embossing times.

	$d_{MAX}$ (nm)		$T_0$ (°C)		$s$ (nm/°C)	
	5 min	15 min	5 min	15 min	5 min	15 min
SC (n-PrNH <sub>2</sub> ) as-prepared	159.3±4.5	158.4±3.6	84.4±0.9	81.0±0.8	4.43	4.15
SC (n-PrNH <sub>2</sub> ) annealed	158.9±4.3	157.1±4.9	130.0±0.6	120.2±0.8	7.94	8.59
SC (n-HexNH <sub>2</sub> ) as-prepared	155.6±5.7	155.1±2.8	110.5±0.7	102.8±0.4	10.24	8.61
SC (n-HexNH <sub>2</sub> ) annealed	159.7±7.4	163.7±8.3	129.3±0.8	120.7±0.8	9.03	10.28
Thermally evaporated	157.1±3.4	156.3±2.8	190.4±0.4	176.9±0.4	10.67	8.37

Values of parameter  $d_{MAX}$  prove that grating in maximal depth can be prepared in all studied thin films within the applied temperature and time range. Maximal depth values are consistently 158.1±2.4 nm.

Decreasing values of  $T_0$  parameter for each set of samples with increasing embossing time is consistent with classical conception of hot embossing – longer embossing times result in deeper imprints (if permitted by the embossing stamp).

Significant differences were observed in values of  $T_0$  temperature in dependence on the thin film deposition method. As-prepared thin films prepared by vacuum thermal evaporation exhibit  $T_0$  value significantly higher than  $T_g$  of the As<sub>33</sub>S<sub>67</sub> ChG ( $T_g$  =145 °C [19]), which is to be expected due to the nature of hot embossing method. Contrary the as-prepared thin films deposited by spin-coating from both n-PrNH<sub>2</sub> and n-HexNH<sub>2</sub> based solutions exhibit  $T_0$  below the  $T_g$ . Identical phenomenon is present even in case of annealed spin-coated thin films.

Possible explanation of observed phenomenon can be found in the structure of studied thin films. Thermally evaporated As-S thin films possess continuous polymer structure mainly based on AsS<sub>3/2</sub> pyramids, As<sub>4</sub>S<sub>4</sub> clusters and S<sub>n</sub> chains and S<sub>8</sub> rings (in dependence on the composition) [21 - 24]. Structure becomes even more polymerized after annealing at elevated temperatures close or above  $T_g$  (embossing process). Transfer of the material necessary for the formation of the surface structure during hot embossing requires classical viscous flow of the material based on bonds cleavage and re-bonding of the materials polymer structure. Thus temperatures significantly above  $T_g$  must be used in order to decrease the viscosity enough to form desired structure under given pressure and time.

On the other hand, source bulk chalcogenide glasses being dissolved in aliphatic amines form nanoclusters in sizes ≤10 nm which maintain structure of the source glass [25, 26]. Polymer structure of the material inside the clusters is terminated on the surface by amine molecules forming alkyl ammonium arsenic sulfide (AAAS) salts [27] (analogy to steric stabilization of nanoparticles [28]). Glass solutions used for thin film deposition by spin-coating method contain amine molecules in two forms: chemically non-bonded molecules and amines bonded to the surface of the clusters. Major part of chemically non-bonded molecules evaporates during formation of the thin film (deposition). Amine molecules bonded in salts

remain within the thin film. AAAS salts can be gradually thermally decomposed at 100 – 110 °C [9] followed by glass clusters bonding and material polymerization [10].

Base on described structural arrangements in thermally evaporated and solution processed thin films, we propose possible explanation of observed notable differences in  $T_0$  parameter: material transport required for the formation of the surface structure during hot embossing in solution processed chalcogenide glass thin films is not based on classical viscous flow (bond cleavage and re-bonding as in case of thermally evaporated thin films) but it is achieved mainly by mutual movement of the glass clusters terminated by ionic salts. From the macroscopic point of view, transfer of the material is viscous flow but atomic principle is significantly different. Measured data are in good agreement with proposed theory:

1) As-prepared n-PrNH<sub>2</sub> based thin films show significantly different behavior to the rest of studied thin film because these thin films were not annealed at the temperature sufficient for AAAS salts decomposition (thin film stabilization at 35°C), glass clusters are terminated by ionic salts and mutual polymerization between clusters is minimal – temperatures well below  $T_g$  are sufficient for hot embossing ( $T_0$  (5 min) = 84.4 °C and  $T_0$  (15 min) = 81.0 °C).

2) Annealed n-PrNH<sub>2</sub> based thin films show significantly increased values of  $T_0$  ( $T_0$  (5 min) = 130.0 °C and  $T_0$  (15 min) = 120.2 °C) because annealing of the thin films induced AAAS salts decomposition and glass clusters became partially interconnected – the structure partly polymerizes.

3) As-prepared n-HexNH<sub>2</sub> based thin films exhibit significantly higher values of  $T_0$  ( $T_0$  (5 min) = 110.5 °C and  $T_0$  (15 min) = 102.8 °C) in comparison with n-PrNH<sub>2</sub> based as-prepared thin films because stabilization of n-HexNH<sub>2</sub> based thin films is done at 115 °C due to the higher boiling point of n-HexNH<sub>2</sub>. Thus AAAS salts are partially decomposed during film stabilization, structure is partly polymerized and higher temperatures are needed for the embossing process.

4) Both n-PrNH<sub>2</sub> and n-HexNH<sub>2</sub> based annealed thin films show identical values of  $T_0$  at 5 and 15 min embossing time because annealing unified structure of the thin films (AAAS salts were mostly decomposed and glass structure significantly polymerized). Nevertheless, material still contains organic residuals in a form of AAAS salts even after annealing [10] so embossing temperature is still significantly lower in comparison with thermally evaporated thin films.

The values of the slope are quite consistent for all studied thin films ~ 8 – 10.5 nm/°C with exception for the as-prepared n-PrNH<sub>2</sub> based thin films which exhibit values of the slope 4.43 and 4.15 nm/°C for 5 and 15 minutes respectively. Observed inconsistency of as-prepared n-PrNH<sub>2</sub> based thin film is probably connected with high content of AAAS salts and low embossing temperatures. Similar slope values of thermally evaporated and spin-coated thin films (excluding as-prepared n-PrNH<sub>2</sub> based thin films) suggests that viscosity of thermally evaporated and “macroscopic” viscosity of solution processed thin films exhibit nearly identical steepness of the temperature dependence at individual temperature ranges.

#### 4. Conclusions

Presented paper provides evidence that solution processed As<sub>33</sub>S<sub>67</sub> chalcogenide glass thin films can be structured by hot embossing method at significantly lower temperatures in comparison with their thermally evaporated counterparts. Observed phenomenon can be explained by different origin of viscous flow of the material. Transfer of the material in the thermally evaporated thin films is based on bond cleavage and re-bonding. Contrary solution processed thin films partially retain the cluster based structure of the glass solution in aliphatic amines. The presence of AAAS salts on the surface of the cluster together with low degree of the structure polymerization between clusters results in significantly reduced embossing temperatures. Founded on our proposed explanation this effect should be general to other chalcogenide glass systems, which would allow wider range of high- $T_g$  chalcogenide glass compositions to be structured using standard soft PDMS stamps without their deformation or destruction. Also substrates

with lower temperature stability could be used for thin film deposition. These effects would simplify embossing process and tailoring of optical properties of the structured materials according to the desired application.

## Acknowledgement

Authors appreciate financial support from grant LM2018103 from the Ministry of Education, Youth and Sports of the Czech Republic and European Regional Development Fund-Project “High-sensitive and low-density materials based on polymeric nanocomposites – NANOMAT” (CZ.02.1.01/0.0/0.0/17\_048/0007376).

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