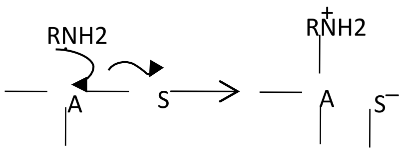
Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

1- Dissolution of ChG in Amine solvent

Ethanolamine (ETA) and Ethylene di-amine (EDA) have been used as the solvent for As_2S_3 and As_2Se_3 glasses. When As_2S_3 glass is dissolved in amines, the solvent acts on the defect sites of the As_2S_3 and breaks it in small clusters and distributed in all over the volume of the solvent. Chern et al. have investigated the dissolution mechanism of As_2S_3 in n-propylamine and n-butylamine and suggest that the reaction is initiated by an electrophonic substitution of a sulphide atom by alkyl amine group (eq. 1) as the lone pair of electron in N attacks As center and cleaves the As-S bond [1]. The overall dissolution process is shown in the (eq. 2), in which the insoluble alkyl amino arsenic compound precipitates out. The remaining product decomposes further under low-temperature baking to give a hydrogenated arsenic sulfide intermediate, as in eq. 3 [1]. Chern et al. also suggest that the high temperature annealing at about 130 °C starts the elimination of H_2S gas and leaving behind a material similar to the bulk ChG as shown in eq. 4.



(1)

$$(3+x)As_2S_3 + 12xRNH_2 \rightarrow 3As_2S_{3+x}(RNH_3^+)_{2x} + 2xAs(RNH)_3\downarrow \quad (2)$$

$$As_2S_{3+x}(RNH_3^+)_{2x} \xrightarrow{80-90°C} As_2S_{3+x}H_{2x} + 2xRNH_2\uparrow \quad (3)$$

$$As_2S_{3+x}H_{2x} \xrightarrow{>130°C} As_2S_3 + xH_2S\uparrow \quad (4)$$

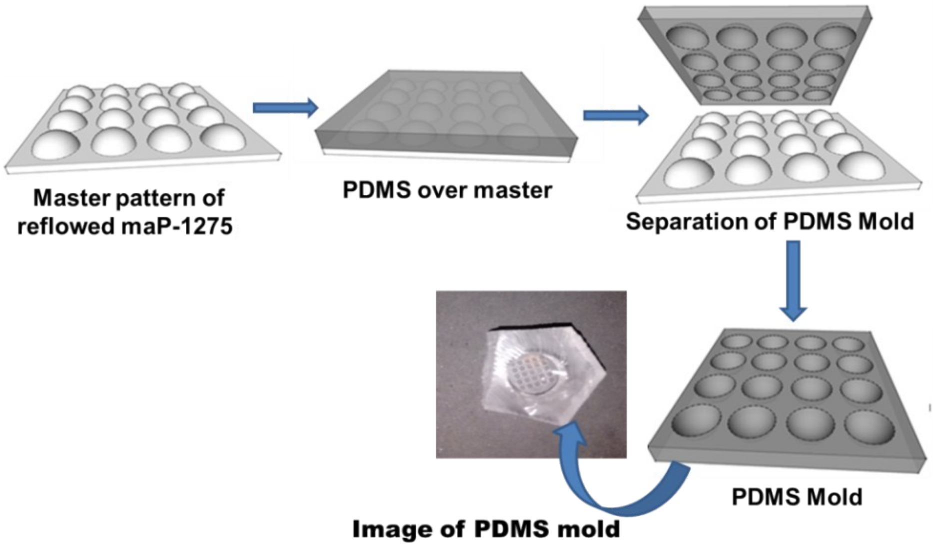
Later, Guiton and Pantano investigated the dissolution mechanism of arsenic sulfide in EDA solvent; they claimed the existence of polymer like chain of As_4S_4 rings bridged by sulfur atom but completely ruled out the formation of alkyl ammonium salt of hydrogen sulfide in the solution [2, 3]. This different mechanism is possible only due to the chelating nature of di-amine solvent.

ETA, we expect, also follows the same mechanism as suggested by Chern. It has –OH terminal group which draws some electron density from the amine group due to high electronegativity of oxygen causing slight decrease in basicity, however has a high polarity value (37.7 F/m) which stabilizes the solute and takes part in hydrogen bonding which results in the high viscous solution desirable for thicker films. It has been found that dissolution rate follows the solvent polarity rather than solvent basicity when comparing the dissolution across multiple solvents [4].

2- Preparation and details of PDMS moulds

Moulds used to create microlens of ChG are made of PDMS and are fabricated by replicating a Microlens array (MLA) stamp via soft lithography. Master pattern is made of reflowed ma-P 1275 and has microlens array of diameter 100 µm and height 50 µm. This master can be prepared using techniques followed in reflowing of photoresist [5].

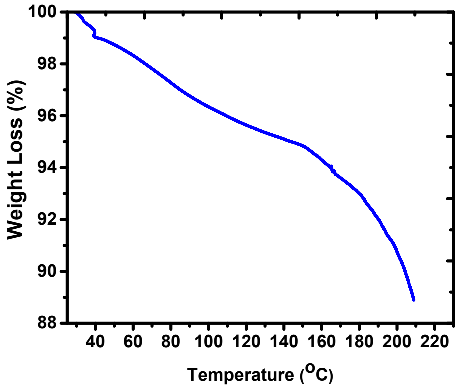
PDMS is prepared by mixing Sylgard 184 and curing agent in 10:1 ratio (by weight) thoroughly. This mixture is kept in a vacuum desiccator for 10 minutes to remove the air trapped in the viscous solution. This mixture is poured on top of MLA stamp gently and cured at 80°C for 2 hours. Negative PDMS replica of MLA is then carefully separated from the master and cleaned for use in ChG MLA generation. A schematic representation of this soft lithography process is shown blow.



Schematic representation of forming PDMS moulds using soft lithography

3- TGA of solution processed films

A thermogravimetric analysis (TGA) on As_2S_3 film is performed. Firstly, the As_2S_3 film is pre-baked at 40°C-45°C for 10 hours and then chalcogenide material is scraped from glass substrate for analysis. TGA instrument used for characterization is TA instruments New Castle, DE 19720, USA, Model No: SDT Q600. The analysis is performed on 10 mg sample in temperature range from 25°C to 200°C at 2°C/min in inert atmosphere as shown in the figure below.



Thermogravimetric analysis of As_2S_3 spin coated from ETA solution, sample pre-baked at 40°C for 10 hours.

We observed a considerable weight loss of about 10 % in the temperature range from 40°C-200°C. Weight loss till 150°C is mainly due to the loss of amine and further weight loss in the sample after 150°C is attributed to the loss of H_2S and residual solvent present in the sample [6]. This is also consistent with our previous work [7], where a FTIR analysis at different annealing temperature was performed to verify the presence of residual solvent in the film at every step and its transmission loss in infrared range.

References:

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4. Nathan A. Carlie, A solution-based approach to the fabrication of novel chalcogenide glass materials and structures. Thesis, Clemson University, 2010.
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6. Song, S., Dua, J., & Arnold, C. B, Influence of annealing conditions on the optical and structural properties of spin-coated As_2S_3 chalcogenide glass thin films, *Optics express*, *18*(6), 5472-5480, 2010.
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