Solution-processing of thick chalcogenide-chalcogenide and metal-chalcogenide structures by spin-coating and multilayer lamination

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Abstract: This paper presents a new technique for fabricating thick (>10um) chalcogenide multilayer structures. Films of arbitrary thicknesses are readily achieved through spin-coating, lamination and baking. For homogeneous systems, layer interfaces can be effectively removed by annealing above Tg. Alternatively, heterogeneous multilayer films can be realized by introducing layers of different chalcogenide materials or metals. In particular, photo-induced Ag dissolution is verified in a laminated multilayer film, with a refractive index increase greater than 0.2. The work presented here has great implications for chalcogenide deposition with potential applications in data storage, IR detection and IR beam combining.

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OCIS codes: (160.2750) Glass and other amorphous materials; (310.1860) Deposition and fabrication.

References and links


1. Introduction

Chalcogenide glasses are well known for their unique optical properties and versatile photo-induced phenomena [1–4], which makes them popular candidates for many optical applications. A number of amorphous chalcogenide materials, including As$_2$S$_3$, have excellent infrared transmission, high refractive index and nonlinearity, which are essential for IR detection and fabricating IR optical components [5–9]. Upon exposure or current injection, photo-electric reactions such as photocristallization, photopolymerization, photodissolution and electromigration can take place [10–13]. Consequently, physical properties including refractive index, absorption coefficient, nonlinear optical susceptibility, resistance, crystal structure and morphology can be modified from the original glass [14,15].

In many applications, well-controlled thicknesses of chalcogenide layers over large distances are critical to device performances. In fact, thick layers are desired for a number of uses. For instance, in fabricating Bragg gratings for holographic data storage, the diffraction efficiency increases with the reflector thickness [16]. In the case of 3D optical data storage with femtosecond lasers, where layers of data are stacked upon one another and separated by 5-100µm, a larger film thickness essentially increases storage capacity per disc [17]. Similar to the ‘deep-depletion’ technology [18], a thick chalcogenide layer may also be applied on CCD arrays to effectively increase the absorption path length, thereby improving the detector sensitivity.

One approach that has been used successfully to create arbitrarily thick layers and multilayers of organic (or composite) materials is spin-coating and laminating multiple layers [19,20]. In the realm of chalcogenide materials, spin-coating has been widely used by researchers to produce functional structures such as waveguides and tunable claddings [4,21,22]. Compared to conventional methods such as vacuum coating (thermal evaporation or sputtering) [23] or pulsed laser deposition [24], solution methods can generally achieve a larger range of thicknesses [25,26] over large areas in a time and cost effective manner. Furthermore, there is the potential to reduce or eliminate intrinsic and/or thermal mismatch stresses that occur during growth and annealing of these traditionally deposited films leading to film delamination [25,27–29].

Combining spin-coating with lamination to create thick films has a number of benefits over monolithic or multilevel spin approaches. Repeatedly spin-coating multiple layers to achieve a thick film is impractical due to the redissolution that occurs as one attempts to spin-coat with the same solution. Furthermore, the lamination technique allows for the fabrication of heterogeneous multilayer structures, which have significant importance to many applications. One example is phase-change memory devices based on the principle of photo-induced or electro-induced metal dissolution. Switching between amorphous and crystalline states has been reported in multilayer structures of two different chalcogenide materials [30,31] or chalcogenide-Ag [32–34].

In this paper, we present a low-cost fabrication process that can deposit chalcogenide films of arbitrary thicknesses via lamination of solution-processed thin chalcogenide films. Homogeneous multilayers, heterogeneous multilayers composed of different chalcogenide materials or metal-chalcogenide hybrids can be achieved. Ag dissolution in spin-coated and laminated chalcogenide films is demonstrated in order to verify the photo-response of such structures with a positive refractive index increase above 0.2 found. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) are also used to characterize the cross-section and transmission spectra in visible and infrared wavelength are analyzed.

2. Experimental

Amorphous As$_2$S$_3$ (metal basis) pieces are dissolved into propylamine and As$_2$Se$_3$ pieces are dissolved in ethylenediamine (EDA) solvent, both at a concentration of 0.8mol/L to obtain the
stock solutions. The dissolution process usually takes a day with a magnetic stirrer to expedite this process. Throughout the process, the solution is kept inside a sealed glass container to minimize solvent evaporation. With the help of a glove box, exposure of the solution to oxygen and moisture is kept to a minimum throughout the preparation procedure since water can lead to precipitate formation [35]. The solution is passed through 0.1µm size filters before being spin-coated on a substrate. To minimize pore formation during subsequent processing, 10% EDA can be added to the solution [36].

Following dissolution, films are spin-coated and laminated following the steps outlined in Fig. 1. The substrate is spun at 1000rpm for 10 seconds. For substrate choices, we use silicon wafers for ellipsometry measurement and SEM study, lithium niobate for infrared spectroscopy measurement, glass microscope slides for optical spectroscopy, or polished NaCl disc substrates for multilayer lamination experiments. Films prepared under these conditions typically have thicknesses around 2µm. By varying the solution concentration and spin conditions, we can spin films of thicknesses up to about 6µm. The resulting films are soft-baked under vacuum at 60°C for 1 hour to remove most of the solvent and then hard-baked at 120-180°C for up to 6 hours to remove excess solvent and further densify the glass [37,38]. After heating, samples are cooled down to room temperature by turning off the heating element and allowing the oven to reach ambient temperature. When making heterogeneous structure, metal layer evaporation is carried out in a clean room facility with a Denton/DV-502A E-Beam Evaporator.

![Fig. 1. Spin-coating and lamination steps for fabricating chalcogenide multilayer structures (a) Spin-coat solution-dissolved chalcogenide onto a piece of NaCl substrate (b) Soft and hard baking to remove solvents (c) [optional] Evaporate a metal layer onto the solidified chalcogenide film (d) Dissolve the NaCl substrate in water to detach films (e) Stack films on top of each other to obtain multilayer structures (f) Post-bake or anneal at a high temperature.](image)

To create multilayer structures without brittle fracture associated with free standing thin chalcogenide films, we begin with a spin-coated film on a non-dissolvable substrate (e.g. Si wafer, LiNbO₃, glass slide) on which we place a spin-coated film supported on the NaCl. This substrate assembly is transferred to a beaker of purified DI water to dissolve the salt substrate. The remaining multilayer can be compressed to remove residual air or water pockets between the layers. Additional layers are then incrementally added in this fashion until the desired number of layers is achieved. Finally, multilayered samples undergo either post-baking at 50°C for 1 hour or annealing at 200°C for 1 hour to study the effects of temperature difference on the interface. The samples are cooled to room temperature in the same manner as described above. SEM images are taken with a Quanta 200 FEG environmental SEM at 15keV high vacuum mode. Compositional analysis and elemental mapping is done with an EDX system.
Film thickness is measured with an Olympus Laser Confocal Microscope, LEXT OLS4000. Refractive index is measured with a Gaertner L3W16 ellipsometer. Infrared transmission spectra of the films are measured with a Nicolet Fourier transform infrared (FTIR) spectrometer using a cooled mercury cadmium telluride detector with a resolution of 4cm$^{-1}$. The UV-VIS transmission spectra are measured with an Ocean Optics HR4000 high-resolution spectrometer.

Photo-induced Ag dissolution into chalcogenide layer is performed with a broadband light source (150W, IR filter) and a red laser (<0.5mW) inside a glove box maintained with minimum oxygen and moisture content. The exposure time for the refractive index measurement is 0.5 hours.

3. Results and discussion

Multilayer lamination enables one to arbitrarily increase layer thickness or introduce new material layers. For instance, Fig. 2 shows the thickness measurement of a four-layer structure before annealing. A total thickness of about 16µm is measured with each layer approximately 4µm. The RMS surface roughness of our spin-coated films was measured to be 0.75nm [39]. After annealing, films adhere strongly to all the substrates and survive repeated ‘scotch tape’ adhesion tests.

Multilayer lamination also alleviates problems associated with removing residual solvent from the films. As spin-coated layers increase in thickness, it becomes progressively harder to remove all solvent. Through the multilayer lamination method for thick films, individual layers can be more thoroughly baked before lamination and the structure as a whole retains less solvent. Such a comparison is demonstrated Fig. 3(a) for monolithic and multilayered films with layer thickness of 4µm. Each data point is taken from the lowest transmission portion of the corresponding FTIR spectrum such as those shown in Fig. 3(b). The absorption at 2950cm$^{-1}$ (3.38µm) is associated with the aliphatic C-H stretch in residual propylamine solvent [37]. Under the same baking condition and total thickness, multilayer structures demonstrate greater transmission and thus less residual solvent in the films. The solid line in Fig. 3(a) corresponds to an exponential fit of the data with an absorption coefficient of 7x10$^{-2}$ µm$^{-1}$. The quality of the fit to the multilayer data suggests a minimal contribution of interfaces to the overall absorption loss. Conversely, the single layer films exhibit linear behavior (dashed line) indicating an increasingly greater absorption due to residual solvent as the film thickness increases.

As shown in the complete FTIR spectra of Fig. 3(b), optical transmission windows below 2.9 µm and above 3.6 µm exhibit transparency greater than 95%. Thus these thick films are...
viable for IR applications within these windows. Within the solvent absorption band, it is possible to significantly increase the transmission by increasing the annealing temperature to the glass transition temperature as shown in the prior literature [37].

Fig. 3. FTIR spectra of multilayer films and extracted transmission valleys. Films are annealed at 150°C for 13 hrs. (a) Lowest transmission of single and multilayer structures plotted against total film thicknesses. Dashed line is a linear fit and solid line is an exponential fit. (b) Full FTIR spectra of multilayer structures.

Further verification of the film quality in the spin-coated/laminated thick films can be found in the SEM. We observe that interfaces between the layers are removed by the annealing step. Figure 4 shows the cross section of a laminated film on top of a spin-coated film with (right) and without (left) being annealed above T_g. This sample was produced by cleaving the film and substrate. We find that the films can be cleaved at room temperature without any delamination which enables the direct coupling of light into and out of these thick films. As densification takes place [37], the total thickness decreases from 3.60µm to 3.41µm, while the material composition remains almost unchanged. EDX analysis on the films indicates a uniform distribution of both As and S throughout the cross section and a ratio that is consistent with the stoichiometry.
Fig. 4. Left: Films with no annealing shows an interface in the middle; Right: Interface removed with annealing at 200°C.

When the newly laminated layer is different from the host material, a heterogeneous multilayer structure can be achieved. Lamination is critical in this process because direct spin-coating will only redissolve the previously-spun layers, making thick multilayer structures impossible. Figure 5 (left) shows a double-layer structure of arsenic sulfide and arsenic selenide by the lamination technique. EDX analysis in Fig. 5 (right) characterizes the interface. Beyond 1µm from the interface, material composition is shown to be pure arsenic sulfide and arsenic selenide as expected. Although near the interface it appears that there could be a diffusion region extending for approximately 1µm to either side, we note that the EDX analysis method used for this data averages over a similar length scale and therefore it is not possible to conclude the presence of significant diffusion. Given that the sample is only annealed at 120°C for 2 hours this result is reasonable as one would expect little solid-state diffusion to occur under this temperature/time combination.

Another technologically important multilayer structure is one containing alternate thin metal layers within the chalcogenide. These structures find importance in plasmonics or high contrast photodarkening and photodoping used in applications ranging from electrochemical systems to optoelectronics and data storage [40]. In particular, Ag doped chalcogenide is one of the most widely studied systems. Multilayer lamination and photo-diffusion can effectively enhance the control and depth of Ag diffusion as well as index modulation at any depth in a
thick structure. In Fig. 6, such fabricated structure is shown, demonstrating a uniform contact between the chalcogenide and Ag layer.

![Cross-sectional SEM of 200 nm thick Ag (thin white layers in the middle) and As$_2$S$_3$.](image)

We test the photo-response of our multilayer structure by depositing a 20nm thick silver layer laminated between two layers of As$_2$S$_3$. Broadband illumination for 10 minutes causes complete silver dissolution into the surrounding. The time resolved spectrum Fig. 7 (left) with the transmission level at 700nm plotted against exposure time in Fig. 7 (right). Transmission rapidly increases for the first 3 minutes before tapering down as the amount of silver fully dissolves. This trend is in general agreement with other published work on thin films [40,41].

![Visible transmission spectrums of Ag dissolving into laminated As$_2$S$_3$ layers at different exposure intervals](image)

Fig. 7. Left: Visible transmission spectrums of Ag dissolving into laminated As$_2$S$_3$ layers at different exposure intervals; Right: Transmission level at 700 nm extracted from the left graph and plotted against exposure time.

The increase in transmission over illumination time indicates a change in refractive index, which is verified by directly measuring the index of refraction of a single Ag layer on top of a single chalcogenide layer. We note that both broadband and green laser produce a net change in the index, whereas a red laser does not. This result is consistent with the need for above band gap illumination to initiate the bond-breaking and doping process [42]. The refractive index (at 632.8nm) of the illuminated area is measured to be $2.41 \pm 0.04$ with broadband illumination as compared to a measured index of $2.16 \pm 0.07$ for non-illuminated spin-coated films. This increase with Ag photodoping is comparable and consistent with other published work using traditional film preparation methods [26,34].

4. Conclusions

In this paper, we have demonstrated the feasibility of fabricating thick metal-chalcogenide and chalcogenide-chalcogenide multilayer structures via a spin-coating and lamination method.
We have shown that these films exhibit regions of high transmission in the IR and that annealing above the glass transition temperature can effectively remove the interface. The photo-response of our multilayer structures is verified through photo-induced Ag dissolution into laminated films and shows a refractive index increase of more than 0.2. This new fabrication method proves its value as a low-cost and efficient way to produce large area chalcogenide layered structures, which are useful in areas such as 3D optical memory device, IR beam combiner, IR detectors and waveguides.

Acknowledgments

The authors would like to thank Dr. Edeline Fotheringham from Daylight Solutions for valuable discussions. This work is supported by the AFOSR/Daylight solution SBIR contract number FA8650-12-M-1430 as well as the National Science Foundation through the MIRTHE Center (Grant No. EEC-0540832).