Solution processed Ge$_{20}$Sb$_5$S$_{75}$ thin films: the effect of solution concentration and multiple layers stacking

STANISLAV SLANG, $^{1,*}$ PETR JANICEK, $^{2,1}$ KAREL PALKA, $^{3,1}$ AND MIROSLAV VLCEK $^{1}$

$^{1}$Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Studentska 95, Pardubice 53210, Czech Republic
$^{2}$Institute of Applied Physics and Mathematics, Faculty of Chemical Technology, University of Pardubice, Studentska 95, Pardubice 53210, Czech Republic
$^{3}$Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentska 95, Pardubice 53210, Czech Republic
$^{*}$stanislav.slang@upce.cz

Abstract: Ge$_{20}$Sb$_5$S$_{75}$ thin films with high chemical resistance to aliphatic amines were deposited from solutions of various glass concentrations (0.015-0.09 g of grinded glass material/ml of n-butylamine) by the spin-coating technique. As-prepared and annealed thin films were analyzed by spectroscopic ellipsometry and EDS (energy-dispersive X-ray spectroscopy). Results proved that the refractive index of thin films was not affected by the solution concentration (within studied range), and the studied optical properties of deposited samples were homogenous in their volume. The Ge$_{20}$Sb$_5$S$_{75}$ solution of the highest concentration (0.09 g/ml) was chosen for deposition of thicker chalcogenide glass material using multiply deposition/thermal stabilization procedure. Prepared multilayers proved to have good optical quality and homogenous chemical resistance through the whole thickness. No interfaces between layers were observed from etching kinetics and SEM scans. Thus, the results confirmed that multiple layers stacking procedure is suitable for deposition of thick homogenous Ge$_{20}$Sb$_5$S$_{75}$ thin films.

© 2019 Optical Society of America under the terms of the OSA Open Access Publishing Agreement

1. Introduction

Chalcogenide glasses (ChGs) are important semiconducting materials with applications especially in IR optics, optoelectronics and photonics [1–3]. They possess high refractive index and wide IR transparency window, which make them unique in comparison with other commercially produced glasses. Besides bulk material application (e.g. lenses, fibers, windows, etc. [2–4]) the ChGs can be deposited as amorphous thin films by vapor or solution based deposition techniques. The ChG thin films were recently successfully used for preparation of stretchable optical devices [5]. Furthermore, scalable fabrication techniques for production of passive large-scale arrays of optical elements were developed [6]. The vapor deposition techniques (e.g. thermal evaporation, laser ablation, sputtering, etc. [7–11]) are traditionally more frequently used and they usually produce thin films with good optical quality. However, sometimes the fractionation of deposited material can occur (especially during thermal evaporation [8,12]) and vacuum based deposition techniques aren't suitable for preparation of thin films doped with thermally or vacuum unstable materials or for preparation of composite materials (e.g. ChG thin films doped with semiconductor luminescent nanoparticles [13,14]).

Solution based deposition techniques (e.g. spin-coating, spiral bar-coating, dip-coating, electrospray, etc. [13–18]) exploits solubility of ChGs in volatile alkaline solvents. Their main advantage lies in simplicity of preparation method, which is reflected in low cost instrumentation. Due to the well-developed commercial printing techniques, the solution based deposition route
has high potential for quick, cost effective mass production of ChG thin films. The main drawback of solution processed ChG thin films is presence of residual solvent molecules [15,16], which affects their physical and chemical properties. Significant portion of solvent residuals can be removed by post-deposition thermal treatment, but this process can be hindered by high thickness of ChG thin film. Strizik et al. [19] reported that thick (∼3 µm) spin-coated chalcogenide glass thin films stabilized by annealing close to the $T_g$ have gradient of optical properties due to the transversal distribution of residual amine solvent through deposited thin films. The thermal stabilization induces formation of organic residuals depleted surface which acts as diffusion barrier for other organic residual molecules inside annealed thin film. The gradient of optical properties can be significantly reduced by hard baking close to softening temperature of ChG but at cost of thin film degradation. However, the gradation of optical properties within their thickness was not observed in thinner spin-coated ChG thin films [20,21]. This fact bring up a question how to prepare thick ChG solution-processed thin films without gradient of optical properties.

One possible way to overcome this problem would be stacking of multiple thinner ChG thin films. Santiago et al. [22] prepared ChG amine salts which were subsequently dissolved in amide solvent. Prepared solution was used for spin-coating of multilayers since amide solvent could not dissolve stabilized ChG thin film. Zha and Arnold [23] used NaCl disc substrates on which they deposited ChG thin films. The films were thermally stabilized and put together in deionized water. The NaCl substrate was dissolved, stacked ChG thin films were compressed and whole process was repeated.

In presented work, we have tested another way of multiple layers stacking which exploits high chemical resistance of thermally stabilized Ge$_{20}$Sb$_5$S$_{75}$ thin films to aliphatic amines [16]. No similar high chemical resistance was found for studied solution processed thin films in As-S nor Ge-S systems [20,24]. 5 at. % substitution of Ge with Sb in Ge$_{25}$S$_{75}$ thin films increased chemical resistance to BA etching solution approx. 23 times [16]. This allows to directly deposit several Ge$_{20}$Sb$_5$S$_{75}$ thin films onto each other from the same n-butylamine solution which would be easier from point of ChG solution manipulation and there would not be a problem with possible hydrolysis of prepared ChG thin films in aqueous solution. The additional advantage of chosen composition and whole Ge-Sb-S system is its non-toxicity, which makes it suitable for potential practical applications. The aim of our research was to find a suitable ChG solution concentration to prepare thick multilayer material with homogenous optical properties and low content of organic residuals.

### 2. Experimental details

Source bulk Ge$_{20}$Sb$_5$S$_{75}$ chalcogenide glass (ChG) was prepared by standard melt-quenching method. Pure 5N elements were weighted into clean quartz ampule in calculated amounts and sealed under vacuum (approx. 10$^{-3}$ Pa). Loaded reagents were melted in a rocking tube furnace at 950 °C for 72 hours. The ampule with melted glass was quenched in a cold water.

Synthetized Ge$_{20}$Sb$_5$S$_{75}$ ChG was grinded in agate bowl and weighted into glass vials to planned concentrations of 0.015, 0.03, 0.045, 0.06, 0.075 and 0.09 g of ChG powder per 1 ml of n-butylamine (BA) solvent. The vials were sealed and Ge$_{20}$Sb$_5$S$_{75}$ ChG powder was dissolving under rigorous stirring for 48 hours. Prepared ChG solutions were clear without any precipitate or turbidity (Fig. 1).

Thin films were deposited using spin-coating technique. The glass solutions of different concentrations were pipetted onto rotating soda-lime substrates and spin-coated (spin-coater Best Tools SC110-B) in argon atmosphere at 2000 rpm for 120 s. One set of samples was also deposited on clean silicon substrates for EDS measurements. Deposited thin films were immediately annealed at 60 °C (soft baking) on a hot plate for 20 min (hereafter referred as as-prepared thin films). Subsequently, the as-prepared Ge$_{20}$Sb$_5$S$_{75}$ thin films were annealed at
Fig. 1. Prepared $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ ChG solutions. A: 0.015, B: 0.03, C: 0.045, D: 0.06, E: 0.075, F: 0.09 g/ml BA.

210 °C (hard baking) inside argon-filled annealing chamber for another 60 min (Fig. 2). The annealing temperature was chosen with respect to our previous work on this ChG composition; so the obtained findings would be complementary [16].

Fig. 2. As-prepared (A) and thermally stabilized (B) $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ ChG thin films.

In order to study effect of multiple layers stacking another set of thin films was deposited from $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ ChG solution with highest concentration (0.09 g/ml of BA) using the identical procedure as described above. However, thermally stabilized thin films (annealed at 210 °C) were used again as substrates for spin-coating of the same solution (0.09 g/ml of BA). The whole deposition/thermal stabilization process was repeated until 5-stack multilayer was prepared. The samples of 2, 3 and 4 stacked multilayers were also taken during preparation to study the effect of addition of every single deposited $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ layer.

Variable angle spectroscopic ellipsometer (VASE J. A. Woollam Co.) was used for optical characterization of deposited $\text{Ge}_{20}\text{Sb}_5\text{S}_{75}$ thin films and multilayers. The ellipsometer was equipped with an automatic rotating analyzer over the spectral range 210 nm – 1700 nm (UV-VIS-NIR), measuring 30 revolutions with photon energy steps of 0.05 eV at three selected angles of incidence (AOI) (50°, 60° and 70°). Near normal incidence optical reflectance was measured by the same instrument. Optical spectrometer (Shimadzu UV3600) was used for measurements of transmission spectra in the spectral region 190–2000 nm. The measured ellipsometry data were evaluated in WVASE32 software together with transmission spectra as supporting material for
generated data fit. Minimization procedure using the mean square error (MSE) values between measured and generated data was conducted to calculate geometrical parameters and refractive index of deposited thin films and multilayers. Their surface roughness was modeled using Bruggeman type of effective medium approximation of void and layers [25].

The scanning electron microscopy (SEM) scans and elemental composition data were obtained using scanning electron microscope LYRA 3 (Tescan) equipped with EDS analyzer AZtec X-Max 20 (Oxford Instruments). The EDS measurements were performed at 5 kV and 20 kV acceleration voltage on three 400 × 400 µm spots for each studied sample.

Prepared multilayer samples were etched in 0.5 vol. % ethylenediamine solution in dimethyl sulfoxide at 25 °C. Data were evaluated by procedure presented in [26]. The etching curves were analyzed at two wavelengths corresponding to the first interference maximum and the first interference minimum of measured transmission spectra.

3. Results and discussion

3.1. The effect of the solution concentration

The experiments with solutions of As-S system proved, that ChG concentration has a high impact on size of glass nanoclusters/fragments that are final product of bulk ChG dissolution [27,28]. Generally, the size of ChG clusters is increasing with increasing solution concentration. However, the ChG clusters are still very small (several nanometers in diameter [27,28]) which questions the impact of solution concentration on properties of subsequently deposited thin films. According to [19], the thickness of solution processed ChG thin films has also a critical role in formation of organic residuals gradient within their volume. Thus, the set of Ge_{20}Sb_{5}S_{75} solutions with different concentrations (0.015-0.09g/ml) was prepared to study possible formation of organic residuals gradient in thinner ChG films (d < 0.5 µm) and if physical properties of deposited samples would be affected by expected changes in glass clusters size. The thin films were spin-coated from prepared ChG solutions using the same deposition conditions and they were characterized by spectroscopic ellipsometry. The spectroscopic ellipsometry data proved that no studied as-prepared or annealed thin films exhibited formation of refractive index gradient within their thickness and thus the volume of thin film was evaluated as homogenous material. Overall MSE of the fit for solution concentration study was less than 3.8. Calculated optical and geometrical parameters of prepared Ge_{20}Sb_{5}S_{75} thin films are summarized in Table 1.

The thickness of as-prepared Ge_{20}Sb_{5}S_{75} thin films is monotonously increasing with increasing concentration of source ChG solution (Fig. 3 – A). The surface roughness of as-prepared thin films is quite low (bellow 2.3 nm) and it is even slightly decreasing with increasing concentration of ChG solution. However, the refractive index of studied as-prepared samples is practically the same for all solution concentrations (Fig. 3 – B) with average value n_{1550} = 1.755 ± 0.009 (at λ = 1550 nm). Thermal stabilization at 210 °C induced structural changes connected with polymerization of ChG structure and releasing of molecules of BA residuals [16]. This process is reflected in changes of geometrical and optical properties of annealed thin films. The thickness of thermally stabilized samples is significantly decreasing (~ 46%). Such major thickness loss also affects surface roughness of annealed thin films, which varies between 6.5-16.4 nm. The refractive index of thermally stabilized samples is again almost identical for all source solution concentrations (n_{1550} = 1.766 ± 0.015 at λ = 1550 nm) and higher than refractive index of as-prepared thin films. Increase in refractive index of thermally stabilized samples is a result of annealing induced structural changes connected with release of low refractive index organic residuals and increase in compactness of thin film matrix [20]. Based on these findings it is reasonable to assume that the ChG solution concentration and hence size of glass clusters doesn’t influence the optical properties of deposited thin films (within chosen concentration range).

The elemental composition of studied monolayer thin films deposited on silicon substrates was investigated by EDS analysis. The measurements proved that as-prepared thin films
Table 1. Values of Ge$_{20}$Sb$_5$S$_{75}$ thin film’s thickness, surface roughness and refractive index at 1550 nm ($n_{1550}$) determined by spectroscopic ellipsometry

<table>
<thead>
<tr>
<th>Concentration (g/ml BA)</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>$n_{1550}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as-prepared</td>
<td>as-prepared</td>
<td>annealed at 210 °C</td>
</tr>
<tr>
<td>0.015</td>
<td>54.1 ± 0.1</td>
<td>2.3 ± 0.1</td>
<td>1.742</td>
</tr>
<tr>
<td>0.03</td>
<td>22.7 ± 0.6</td>
<td>10.7 ± 0.4</td>
<td>1.934</td>
</tr>
<tr>
<td>0.045</td>
<td>115.2 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>1.768</td>
</tr>
<tr>
<td></td>
<td>63.6 ± 0.1</td>
<td>7.3 ± 0.1</td>
<td>1.968</td>
</tr>
<tr>
<td>0.06</td>
<td>184.9 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>1.762</td>
</tr>
<tr>
<td></td>
<td>107.4 ± 0.1</td>
<td>7.6 ± 0.1</td>
<td>1.975</td>
</tr>
<tr>
<td>0.075</td>
<td>261.3 ± 0.1</td>
<td>0.8 ± 0.1</td>
<td>1.758</td>
</tr>
<tr>
<td></td>
<td>162.5 ± 0.1</td>
<td>6.5 ± 0.1</td>
<td>1.976</td>
</tr>
<tr>
<td>0.09</td>
<td>377.0 ± 0.2</td>
<td>0.7 ± 0.1</td>
<td>1.747</td>
</tr>
<tr>
<td></td>
<td>196.0 ± 0.1</td>
<td>8.5 ± 0.1</td>
<td>1.977</td>
</tr>
<tr>
<td>0.09</td>
<td>439.6 ± 0.2</td>
<td>0.2 ± 0.1</td>
<td>1.750</td>
</tr>
<tr>
<td></td>
<td>238.6 ± 0.2</td>
<td>16.4 ± 0.2</td>
<td>1.964</td>
</tr>
</tbody>
</table>

Fig. 3. Thickness (A) and refractive index at $\lambda = 1550$ nm (B) of as-prepared and annealed Ge$_{20}$Sb$_5$S$_{75}$ thin films in dependence on source solution concentration.

deposited from solutions of higher concentrations (0.045-0.09 g/ml) have average Ge$_{20.1}$Sb$_{4.4}$S$_{75.5}$ composition, which is practically same as planned Ge$_{20}$Sb$_5$S$_{75}$ composition. As-prepared thin films deposited from more diluted solutions (0.015 and 0.03 g/ml) were slightly sulfur depleted with Ge$_{24.2}$Sb$_{5.5}$S$_{70.3}$ composition. However, this difference is most likely caused by experimental error of EDS analysis due to the measurement of very thin films. Annealing of thin films at 210 °C induced slight germanium depletion but their overall Ge$_{18.8}$Sb$_{4.5}$S$_{76.9}$ composition is still close to the planned values.

The EDS measurements proved that samples contain high content of N and C atoms. The origin of N atoms can be unambiguously attributed to the presence of residual BA molecules, because no other sources of N could be expected (spin-coating and annealing in Ar inert atmosphere). The dependence of N:Ge ratio on source solution concentration is depicted in Fig. 4. Similarly as refractive index values, the N:Ge elemental ratio is practically constant within whole studied source solution concentration range. It was confirmed that annealing induces releasing of organic residuals but they could not be completely removed even by annealing at 210 °C. Also, there
are no signs of barrier formation which would hinder release of organic residuals in studied Ge$_{20}$Sb$_5$S$_{75}$ thin films with $d < 0.5$ µm.

**Fig. 4.** The N:Ge elemental ratio of as-prepared and annealed Ge$_{20}$Sb$_5$S$_{75}$ thin films in dependence on source solution concentration. Error bars represent standard deviation from averaged value.

The results of spectroscopic ellipsometry and elemental analysis proved that optical properties and composition of studied Ge$_{20}$Sb$_5$S$_{75}$ thin films was practically the same and independent on used solution concentration. Thus, the thickest samples deposited from the most concentrated solution (0.09 g/ml) was chosen for multiple layers stacking.

### 3.2. The effect of multiple layers stacking

Samples of multifold Ge$_{20}$Sb$_5$S$_{75}$ layers (1-5x) were deposited by repeating spin-coating followed by thermal stabilization procedure and prepared thin films were again analyzed by spectroscopic ellipsometry. Overall MSE of the fit for multilayers study was less than 6.6 using the model of homogenous optical properties. The four samples were prepared in total for each number of deposited layers and averaged results are summarized in Table 2. Data proves that thickness of deposited thin films (Fig. 5 – A) is linearly increasing with increasing number of layers (adj. R-square = 0.99978). It proves that concept of thick ChG thin films deposition using multiple layers stacking from the same source solution is correct. However, it should be stressed again that it can be used only for stabilized solution processed ChG thin films with high chemical resistance to used amine solvent.

**Table 2.** Values of Ge$_{20}$Sb$_5$S$_{75}$ multilayers thickness, surface roughness and refractive index at 1550 nm ($n_{1550}$) determined by spectroscopic ellipsometry

<table>
<thead>
<tr>
<th>Number of layers</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
<th>$n_{1550}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>238.6 ± 5.5</td>
<td>16.4 ± 1.6</td>
<td>1.960 ± 0.007</td>
</tr>
<tr>
<td>2</td>
<td>490.7 ± 7.5</td>
<td>10.3 ± 0.9</td>
<td>1.955 ± 0.006</td>
</tr>
<tr>
<td>3</td>
<td>745.9 ± 5.3</td>
<td>6.8 ± 1.7</td>
<td>1.949 ± 0.003</td>
</tr>
<tr>
<td>4</td>
<td>1021.0 ± 18.5</td>
<td>6.4 ± 0.4</td>
<td>1.942 ± 0.009</td>
</tr>
<tr>
<td>5</td>
<td>1262.3 ± 20.0</td>
<td>4.6 ± 0.4</td>
<td>1.941 ± 0.001</td>
</tr>
</tbody>
</table>

The surface roughness of deposited multilayers is actually decreasing with increasing number of layers, which makes this process even more beneficial in terms of multilayers application in optics. The first thermally stabilized Ge$_{20}$Sb$_5$S$_{75}$ film with the highest surface roughness is coated with another fresh ChG thin film while Ge$_{20}$Sb$_5$S$_{75}$ solution is filling presented grooves or
Fig. 5. Thickness (A) and refractive index at \(\lambda = 1550\) nm (B) of annealed Ge\(_{20}\)Sb\(_5\)S\(_{75}\) multilayers in dependence on number of deposited layers. Error bars represent standard deviation from averaged value.

The smoothening of top layers surface due to its partial dissolution in used amine solvent also cannot be excluded. The refractive index of studied samples is slightly decreasing with increasing number of layers (Fig. 5 – B) but their values are still significantly higher than refractive index of as-prepared Ge\(_{20}\)Sb\(_5\)S\(_{75}\) thin films and still within the range observed in annealed samples prepared from solutions of different concentrations (Fig. 3 – B).

The EDS analysis of multilayer samples proved that the content of sulfur is slightly decreasing with increasing number of layers (Fig. 6). The composition of annealed monolayer was Ge\(_{18.8}\)Sb\(_{4.4}\)S\(_{76.8}\), which is very similar as the average composition obtained in previous solution concentration tests. The 5-layered sample is missing approx. 3 at.\% of sulfur in comparison with planned Ge\(_{20}\)Sb\(_5\)S\(_{75}\) composition. The cause can be an effect of multiple annealing of inner layers of the sample (e.g. ChG material in the first deposited layer is annealed five times while ChG material in top layers only once) and/or some part of sulfur from the top substrate layer is leached during pipetting of another portion of ChG solution. The Ge\(_{20}\)Sb\(_5\)S\(_{75}\) composition has significant sulfur overstoichiometry and thus formation of homopolar S-S bonds can be expected. It was proved [29] that S-S homopolar bonds are highly soluble in aliphatic amines and their partial sulfur leaching during interaction of amine based ChG solution and the top of used Ge\(_{20}\)Sb\(_5\)S\(_{75}\) substrate layer is highly probable.

Fig. 6. The elemental composition of annealed Ge\(_{20}\)Sb\(_5\)S\(_{75}\) multilayers in dependence on number of deposited layers. Dashed lines indicate nominal planned composition.
The thickness dependence of chemical resistance of deposited multilayers was studied by wet-etching in 0.5 vol. % ethylenediamine solution in dimethyl sulfoxide at 25 °C. Obtained etching curves and total etching times are presented in Fig. 7. Data prove that dependence of etching time on number of deposited layers is practically linear (adj. R-square = 0.99941) which corresponds with linearly increasing thickness of deposited multilayers (Fig. 5 – A). The etching curves of prepared multilayers (Fig. 7 – B) show that there is no gradient or step-like changes of chemical resistance within the thickness of stacked multilayers, which is a proof of their structural and compositional homogeneity. This fact corresponds well with the low MSE obtained by ellipsometric data evaluation using model of homogenous optical properties.

**Fig. 7.** Dependence of etching time on number of deposited Ge$_{20}$Sb$_5$S$_{75}$ layers (A) and etching curves of prepared Ge$_{20}$Sb$_5$S$_{75}$ multilayers (B).

The cross-section of prepared 5-layered sample was analyzed by SEM. Typical conchoidal fracture can be observed which is usual for brittle glass materials without any planes of separation (Fig. 8 – A). The cross-section of deposited multilayer is homogenous without noticeable layered structure. The back scattered electron detector signal also did not confirm any elemental mass variations (Fig. 8 – B). Based on obtained results, the homogenous multilayer samples were successfully prepared and multiple layer stacking technique is suitable for deposition of homogenous thicker ChG thin films from the same source solution (if it is permitted by chemical resistance of annealed thin film).

**Fig. 8.** SEM scans of Ge$_{20}$Sb$_5$S$_{75}$ 5-layered sample cross-section – secondary electrons signal (left) together with backscattered electrons signal (right).
4. Conclusions

The Ge$_{20}$Sb$_{5}$S$_{75}$ thin films were deposited from solutions of various concentrations (0.015-0.09 g/ml) by spin-coating technique and subsequently thermally stabilized at 210 °C. The thickness of prepared samples was increasing with increasing ChG solution concentration but refractive index and content of residual solvent were practically unaffected. Annealing induced structural changes connected with releasing of organic solvent residuals and structural polymerization reflected in increase of refractive index and decrease of films thickness. Based on obtained results, the most concentrated Ge$_{20}$Sb$_{5}$S$_{75}$ solution (0.09 g/ml) was chosen for multiple layers stacking and samples of multifold (1-5x) Ge$_{20}$Sb$_{5}$S$_{75}$ layers were deposited. Their thickness was linearly increasing with increasing number of layers while refractive index was slightly decreasing. However, spectroscopic ellipsometry, wet-etching and SEM cross-section of prepared multilayers confirmed that properties of studied material are homogenous within their volume and no planes of separation were observed. Thus, the multiple layer stacking is suitable for deposition of thicker chalcogenide glass films from the same source solution under the condition of high chemical resistance of thermally stabilized material to used amine solvent.

Funding

Grant Agency of the Czech Republic (16-13876S); Ministry of Education, Youth and Sports of the Czech Republic (LM2015082); European Regional Development Fund (CZ.02.1.01/0.0/0.0/17_048/0007376).

Disclosures

The authors declare no conflicts of interest.

References

14. S. Slag, L. Loghina, K. Palka, and M. Vlcek, “Exposure enhanced photoluminescence of CdS$_{0.9}$Se$_{0.1}$ quantum dots embedded in spincoated Ge$_{20}$Sb$_5$S$_{75}$ thin films,” RSC Adv. 7(85), 53830–53838 (2017).


