Supporting Information

for

Thin-film Growth of Low Temperature Lead Antimony Sulfide Plagionite Phases

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Preclusion of hydrogen incorporation

To show that our method precludes hydrogen incorporation, it is necessary to identify the possible sources of hydrogen that may exist during our thin-film process.

1 – the glass substrates: just before being loaded into our UHV system, the substrates are cleaned in IPA and blown dry with compressed N_2. This is one of the standard UHV-compatible cleaning methods. Substrates are then pumped down over night to 10^{-9} Torr, before being transferred to the deposition chamber. No significant amounts of hydrogen or water are present.

2 – film deposition: deposition takes place in a deposition chamber pumped with a cryo-pump to a base pressure of high 10^{-9} Torr – low 10^{-8} Torr. This is an ultra high vacuum environment, and therefore no significant amounts of hydrogen or water vapor are present. The deposition plasma is established using high purity Ar gas, again no significant amounts of hydrogen or water vapor are present.

3 – sample transfer: After deposition and before annealing, samples are rapidly transferred in air, at this stage there is the possibility for adsorption of a water monolayer on the surface of the film. Nevertheless, that monolayer does not represent a significant amount of water nor hydrogen compared to the ~1 μm thick precursor film.

4 – sample storage: Samples are stored in a dry glove-box, with a controlled N_2 atmosphere. Once again, no significant amounts of hydrogen or water vapor are present.

5 – sample annealing: Finally, before annealing, elemental sulfur (stored in the glove-box) and samples are placed in a tube, that is evacuated to 10^{-3} Torr and back-filled with high purity N_2, this purge process is performed 5 times. A final evacuation brings the tube to a pressure of 10^{-3} Torr, just before starting the annealing. Thus, the only residual gas that should be present is N_2. In the worst case scenario that a monolayer of water would be adsorbed on the film at step #3, that monolayer would be desorbed rapidly during the first stage of the annealing (temperature ramp to 400°C).

Therefore, our PVD precursor film deposition followed by annealing under sulfur vapor precludes the incorporation of significant amounts of hydrogen into our films.

Layered precursor films

PbS formation during precursor deposition and thickness range of the repeat bi-layer

Co-sputtering of Pb and Sb_2S_3 experiments were performed. It has been observed that when co-sputtering Sb_2S_3 (100 W − RF) and Pb (10 W − DC), no Sb or S were deposited on the substrate, according to microprobe (WDX) analysis. Therefore co-sputtered films of Sb_2S_3 and Pb can not yield ternary phases of lead antimony sulfides. Considering the geometry of our deposition system, with substrate-directed off-normal sputtering guns, it is believed that the heavier and more energetic Pb atoms scatter away the lighter and less energetic Sb and S atoms. This suggests that, when performing continuous 100 W RF-sputtering of Sb_2S_3 and cycled 10 W DC-sputtering of Pb, the formation of PbS does not occur during the co-sputtering stage, but rather by interfacial reaction of lead with the sulfur contained in the layer of amorphous Sb and S.

To ensure reproducibility of the annealing process and especially of the layer interdiffusion and phase nucleation steps, the repeat bi-layer (amorphous (Sb,S) + crystalline PbS) thickness was kept between 65 and 80 nm, with an approximate PbS layer thickness varying from 45 nm to 60 nm (evaluated from backscattered electron SEM images). This corresponds to an Sb:Pb ratio of 0.74 to 1.54. In that experimental range, the as-deposited precursor films are all composed of amorphous (Sb,S) and crystalline PbS, with crystallite size varying from 9 nm to 13 nm. XRD of the as-deposited precursor films revealed no sign of crystalline lead, suggesting that for 65 to 80 nm thick bi-layers, the interdiffusion of sulfur into the lead layer is complete. Finally, the phases obtained from these precursor films annealed under sulfur vapor at 400°C for 45 to 50 minutes were all plagionite group phases.

PbS crystallite size in the layered precursor films

The PbS crystallite size has been determined from the x-ray line width using the following Scherrer formula:

$$t = \frac{0.9\,\lambda}{\sqrt{B_M^2 - B_S^2}\,\cos\theta_B}$$

where t is the crystallite thickness, λ the x-ray wavelength (1.5418 Å for Cu K$_\alpha$), θ_B the Bragg angle (half the measured diffraction angle), B_M is the width in radians of one of the sample diffraction peaks at half height and B_S is the width in radians of one of the standard diffraction peaks at half height.

The standard peak width B_S should be obtained from a highly crystalline sample with a diffraction peak at a similar diffraction angle to that of the sample. This value represents the instrumental broadening. The standard used was a highly crystalline film of lead with crystallites larger than 1 micron by SEM. The lead (111) reflection at $2\theta_B \sim 31.3°$ was considered and the instrumental broadening was determined to be $B_S = 0.005$ rad.

The PbS crystallite size has been calculated for several precursor films, and especially for the precursor films that yielded the plagionite and semseyite films presented in this paper. The lead sulfide (200) reflection at $2\theta_B \sim 30.1°$ was considered to determined B_M and the crystallite size using the above Scherrer formula. Results are given in the table below. The repeat bi-layer (amorphous (Sb,S) + crystalline PbS) was determined from SEM images and the PbS layer was approximately evaluated from backscattered-SEM images.

	B_M	PbS crystallite size	Repeat bi-layer thickness	PbS layer thickness
Plagionite film precursor	0.017 rad	9 nm	65 nm	45 nm
Semseyite film precursor	0.012 rad	13 nm	70 nm	55 nm

As one can see, for both precursor films, the PbS crystallite size is smaller than the repeat bi-layer thickness or the PbS layer thickness.

Preparation of PbS thin films

Films of PbS (galena) were prepared by sulfurization of Pb films. Pb films were deposited on glass microscope slides via 10 W DC sputtering of Pb at an argon plasma pressure of 66.7 (±0.3) mPa. Once deposited, Pb precursor films were centered in an evacuated tube and annealed under sulfur vapor in a two-zone tube furnace. They were heated at 170°C for 2 hours and then at 300°C for 5 hours. A sulfur flux was generated across the tube as the elemental sulfur was maintained at ~180°C at one end of the tube, while the other end of the tube remained at room temperature.

XRD data collection

The morphology, structure and composition of the films were systematically evaluated via Scanning Electron Microscopy (SEM), area detector collected x-ray diffraction (XRD) and microprobe analysis (WDX). Herein, particular attention will be given to the XRD data. XRD powder patterns were collected with a Bruker-AXS D8 diffractometer equipped with a Cu K_α source collimated with a 0.5 μm pinhole collimator and a GADDS area detector. Films were appropriately Z-aligned with the center of the goniometer, during data collection films were oscillated in X and Y (±1 mm) in order to sample a larger area of the film. The diffracted signal was collected from $2\theta = 3°$ to $2\theta = 85°$.

X-ray diffraction powder pattern

In order to assess the absence of PbS (galena) in the plagionite and semseyite films, it is first interesting to look at the powder pattern obtained from a ~1 μm PbS film (Figure S1). PbS (galena) crystallizes in the face centered cubic Fm-3m space group (225). As is shown in Figure S1, no significant peak position shift can be observed between the experimental film pattern and the reference pattern. The inset of Figure S1 gives the reference reflection positions and relative intensities[1] as well as the experimental reflection positions and relative intensities we observed. Also, it can be seen that PbS produces a strong diffracted signal with a maximum count rate around 1.6 counts per second (cps).

In the plagionite film powder pattern shown in Figure S2, peaks around 2θ values of 26°, 30° and 51° can all be attributed to plagionite phase reflections. Moreover, no diffraction peak can be observed at 2θ values of 43.099°, 53.496°and 68.952°, which would correspond respectively to the PbS (220), (222) and (331) reflections. Thus, the plagionite film is free of a significant amount of PbS.

In the semseyite film powder pattern shown in Figure S3 and its inset, the analysis of the XRD data is a little more difficult, as all the PbS reflections are positioned very close to semseyite reflections. Nevertheless, one notices that at 2θ ~ 26°, the film XRD pattern features a weak peak at 26.15° with a count rate of 0.018 cps. That peak has a position which is more compatible with the semseyite reference pattern. Moreover, considering that it would correspond to the strong (111) PbS reflection, its weak intensity (0.018 cps) tends to prevent attribution of the peaks around 2θ = 43°, 51° and 53.5° with respective intensities of 0.015 cps, 0.018 cps and 0.014 cps, only to PbS, since their intensity would then respectively be 0.013 cps, 0.008 cps and 0.004 cps according to the relative intensities observed (see inset Figure S2). The higher angle peaks (2θ > 55°) also do not provide clear evidence of the presence of PbS. Lastly, microprobe data produce a composition of $Pb_{8.6}Sb_{7.6}S_{21.8}$ for semseyite compared to the ideal $Pb_9Sb_8S_{21}$. Thus, microprobe data indicates that the film is sulfur rich but extremely close to the expected Pb:Sb ratio for semseyite. Therefore, we believe that the obtained semseyite films do not contain a significant amount of PbS.

For both plagionite and semseyite, some differences between the intensities of our films and the standard patterns obtained from geological samples can be observed. These differences can be attributed to some film texture and to some slight displacements of the atoms that can affect the scattering factor and the peak intensity. On the plagionite film XRD pattern, one notices that a few peaks are shifted (< ±0.2°). This can be attributed to slight extension or contraction of the lattice

dimensions, compared to the geological sample used for the reference pattern. These differences between our film XRD patterns and the geological sample XRD patterns used as references are minor.
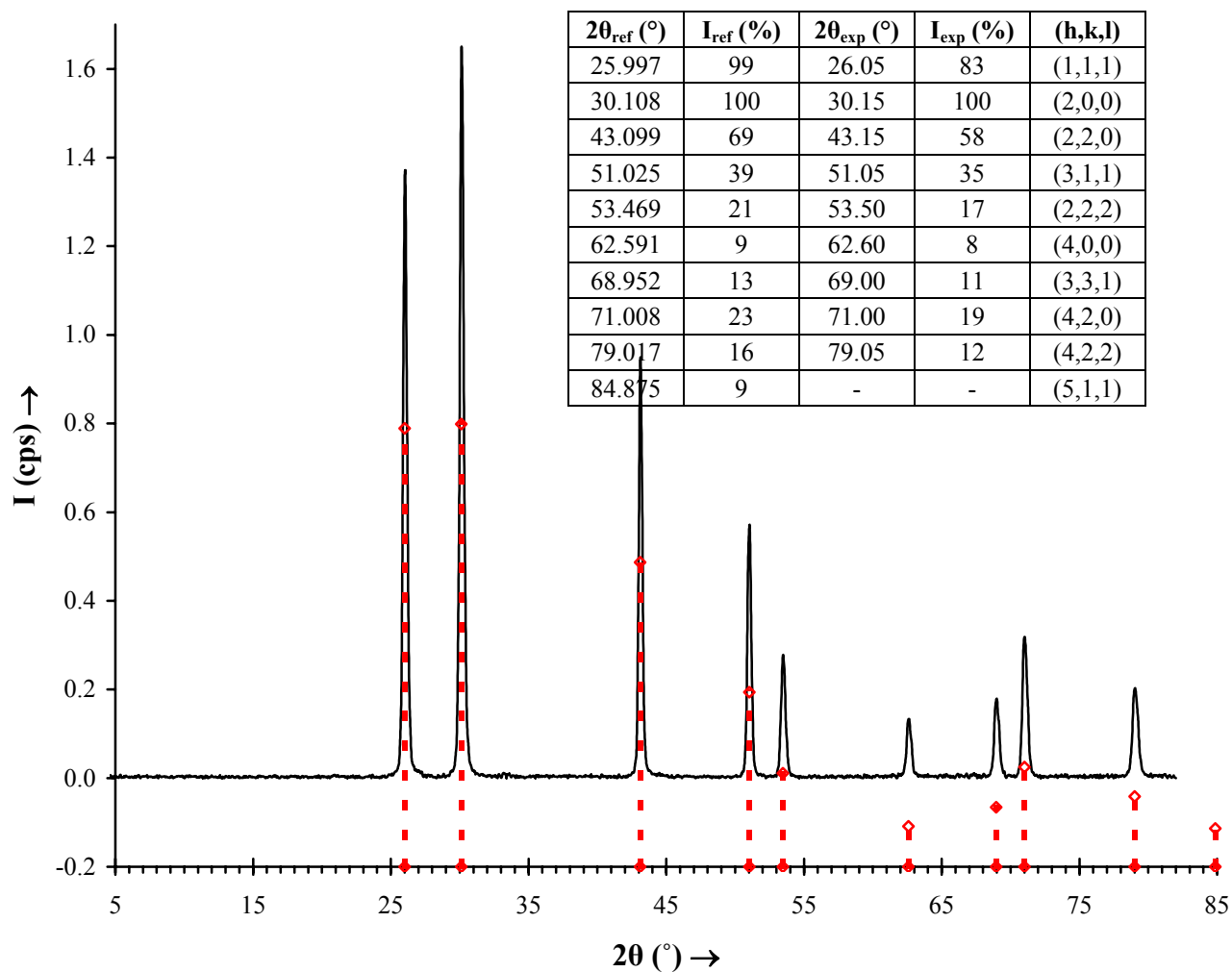
2θ_ref (°)	I_ref (%)	2θ_exp (°)	I_exp (%)	(h,k,l)
25.997	99	26.05	83	(1,1,1)
30.108	100	30.15	100	(2,0,0)
43.099	69	43.15	58	(2,2,0)
51.025	39	51.05	35	(3,1,1)
53.469	21	53.50	17	(2,2,2)
62.591	9	62.60	8	(4,0,0)
68.952	13	69.00	11	(3,3,1)
71.008	23	71.00	19	(4,2,0)
79.017	16	79.05	12	(4,2,2)
84.875	9	-	-	(5,1,1)

Figure S1. Galena (PbS) film XRD pattern and PbS reference pattern.[1] Inset: PbS reference peak positions and relative intensities according to Noda *et al.*[1], experimental peak position and relative intensities and Miller indices.
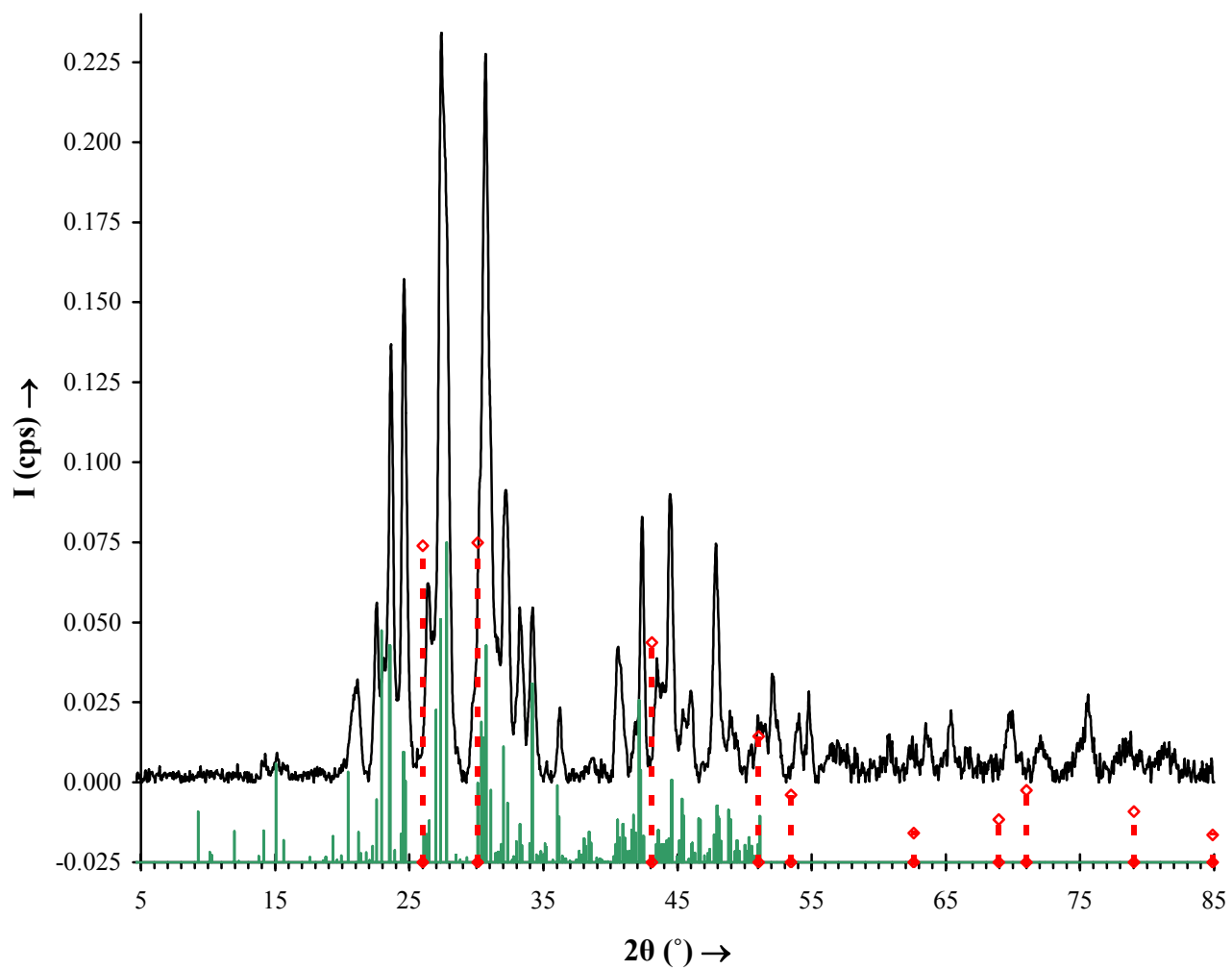
Figure S2. Plagionite ($Pb_5Sb_8S_{17}$) film XRD pattern and reference patterns of plagionite[2] (green solid lines) and PbS (red dashed lines).[1]
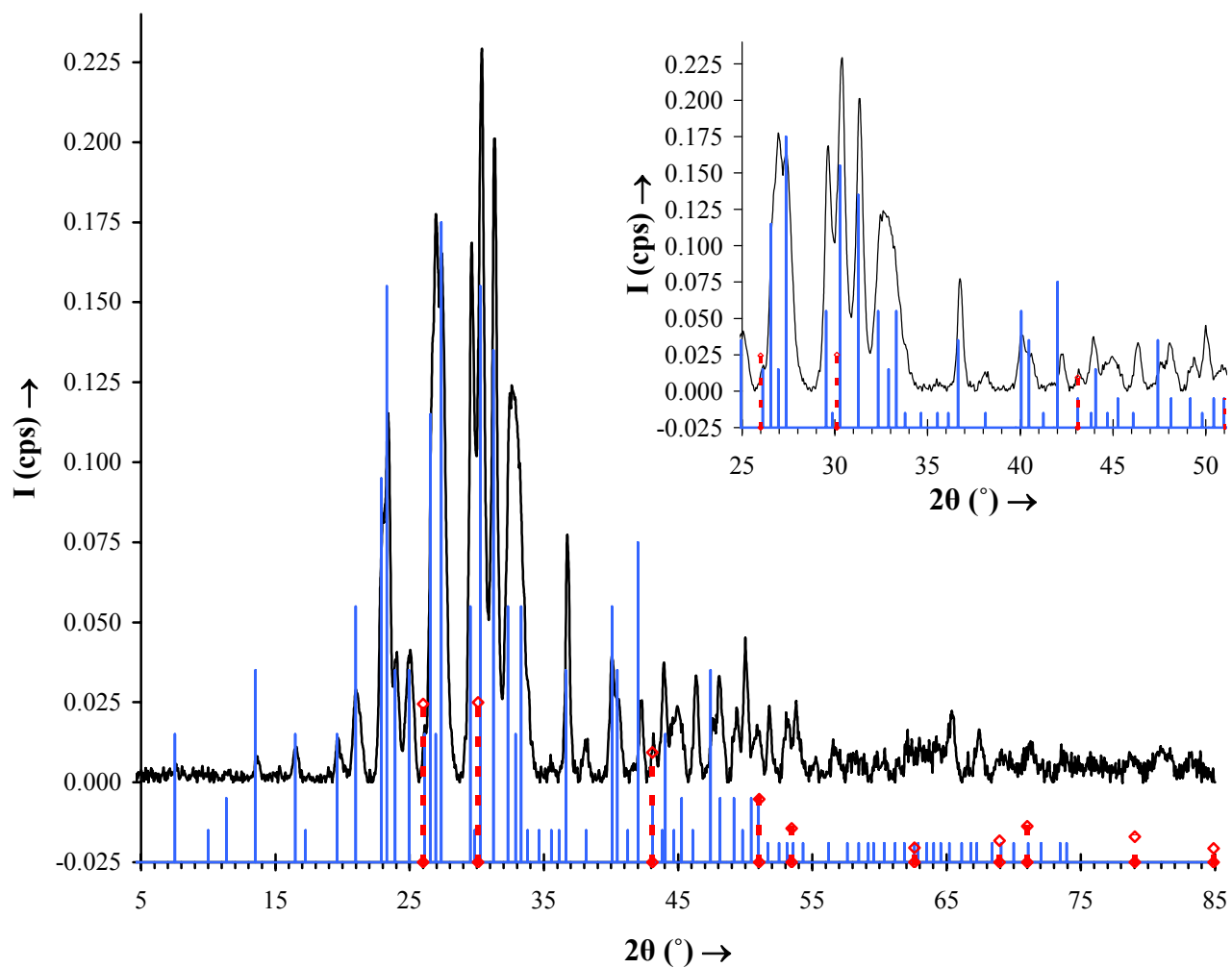
Figure S3. Semseyite ($Pb_9Sb_8S_{21}$) film XRD pattern and reference patterns of semseyite[3] (blue solid lines) and PbS (red dashed lines).[1] Inset: zoom of the $2\theta = 25°$ to $51°$ area.

References:

[1]   Y. Noda, K. Masumoto, S. Ohba, Y. Saito, K. Toriumi, Y. Iwata, I. Shibuy, *Acta Crystallogr., Sect. C* 1987, **C43**, 1443-1445.

[2]   S. -A. Cho, B. J. Wuensch, *Nature* 1970, **225**, 444-445.

[3]   J. L. Jambor, *Mineral. Mag.* 1969, **37**, 443-446.