Thin-film growth of low temperature lead antimony sulfide plagionite phases†

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Smooth and compact $Pb_5Sb_8S_{17}$ and $Pb_9Sb_8S_{21}$ thin films were synthesized *via* sulfurization of unique layered precursor films of amorphous (Sb,S) and crystalline PbS; our syntheses suggest that these plagionite group phases are metastable and indicate that their formation does not require hydrogen incorporation.

Lead antimony sulfides have attracted the interest of numerous mineralogists, because of their chemical and mineralogical complexity, as well as their common association with ore-forming sulfides. Among the numerous lead antimony sulfide phases (at least 18 such phases have been identified), most belong to the so-called acicular phases, which may be synthesized in the laboratory using conventional solid state methods. However, the four phases known as the plagionite group are distinct from the acicular phases; they adopt tabular crystal habits,[1] and share common crystallographic features.[2–5] Moreover, they are relatively rare in nature, and in the laboratory have, until now, been exclusively synthesized under hydrothermal conditions at temperatures near 400 °C. The plagionite phases, both natural and synthetic in origin, decompose into phases stable in the "dry" system upon heating at temperatures above 425 °C.[1,6] Garvin hypothesized that formation of the plagionite group compounds depended upon an additional essential volatile component, probably hydrogen, that would be liberated upon heating.[1] Thus, for over 30 years, the plagionite compounds have been regarded as not existing on the pure Pb–Sb–S phase diagram.

Containing only cost effective and abundant elements, Pb–Sb–S compounds are potential light absorbers for thin-film solar cells. Indeed, with energies close to 1.4 eV,[7,8] their bandgaps are appropriate for efficient solar to electrical energy conversion.[9] Moreover, a recent investigation of the potential of many mineralogical compounds for photovoltaic applications indicated that $Pb_9Sb_8S_{21}$ (semseyite) displayed "device quality" properties.[10] Dittrich *et al.* also reported preliminary thermal evaporation and subsequent characterization of multiphase Pb–Sb–S thin films.[11] Herein we report the synthesis of phase-pure thin films of two members of the plagionite group (plagionite, $Pb_5Sb_8S_{17}$ and semseyite, $Pb_9Sb_8S_{21}$) using methods that preclude the inclusion of hydrogen.

Precursor films were deposited on glass microscope slides *via* magnetron sputtering at an argon plasma pressure of 66.7 ($\pm$0.3) mPa. The layered precursor films were obtained from continuous

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† Electronic supplementary information (ESI) available: Experimental details and XRD patterns. See DOI: 10.1039/b606177j

100 W RF-sputtering of an Sb_2S_3 target (Sophisticated Alloys Inc.) and cycled 10 W DC-sputtering of Pb with different ON and OFF times to achieve target Sb : Pb ratios. Once deposited, precursor films were annealed under sulfur vapor in a two-zone tube furnace. Films were centered in an evacuated tube and heated to 400 °C for 45 to 50 minutes. 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, creating a sulfur flux through the tube.

A typical layered precursor film is shown in Figs. 1a and 1b. The XRD pattern (Fig. 1c) indicates that PbS is the only crystalline phase in these films, and qualitative depth profiling analysis (Fig. 1d), using TOF-SIMS during Ar^+ sputtering of the film, shows that both the sulfur and antimony content vary together.
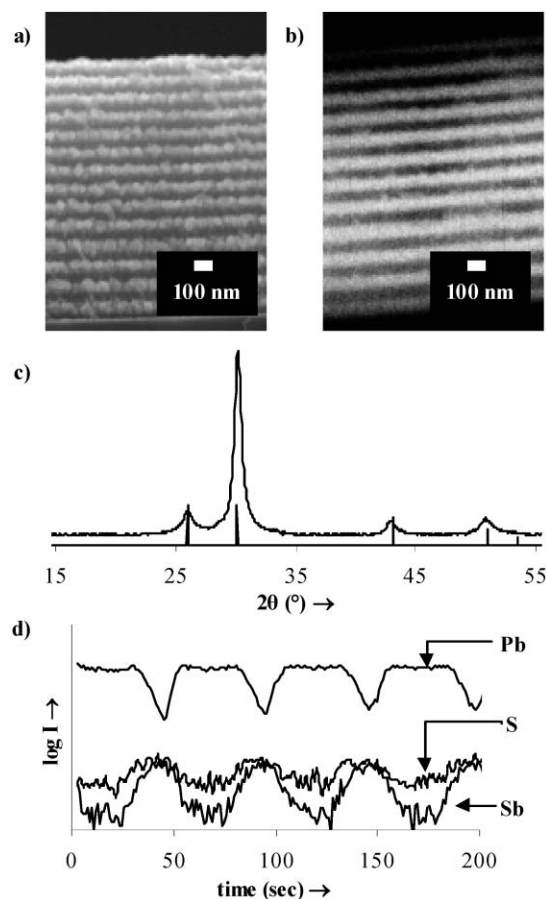

Fig. 1 As-deposited layered precursor films. a) SEM image, b) back-scattered electron image, c) XRD pattern and PbS reference pattern,[17] and d) TOF-SIMS depth profiling analysis.

Therefore, the precursor films are stacks of crystalline PbS layers and amorphous layers containing Sb and S. It has also been noted (by WDX) that when sputtering the two targets (Sb_2S_3 and Pb) simultaneously, no Sb or S is deposited on the substrate. The formation of PbS is believed to occur by interfacial reaction of lead with the sulfur contained in the layer of amorphous Sb and S.

As shown in Figs. 2 and 3, ~1.5-micron-thick films of plagionite ($Pb_5Sb_8S_{17}$) and semseyite ($Pb_9Sb_8S_{21}$) were successfully prepared from precursor films with different ratios of Sb : Pb. XRD data (Figs. 2c and 3c) and WDX data corroborated the phase-pure synthesis of $Pb_5Sb_8S_{17}$ and $Pb_9Sb_8S_{21}$. The thin-film powder patterns match reference powder patterns satisfactorily and indicate the absence of detectable PbS impurities (see supporting information). WDX data yield compositions of $Pb_{5.2}Sb_{7.3}S_{17.4}$ for plagionite and $Pb_{8.6}Sb_{7.6}S_{21.8}$ for semseyite. Moreover, films were continuous and smooth, with mirror-like surfaces. The surface SEM images (Figs. 2b and 3b) show dense film morphology and that films were composed of small crystal grains (0.1 μm or less). Cross-sectional images (Figs. 2a and 3a) show that films were homogeneous throughout their thickness with no evidence of the layered precursor structure. Cross-sectional images of the plagionite film (Fig. 2a) reveal little film porosity and those of the semseyite film (Fig. 3a) show a completely dense film.

Metallic Pb–Sb co-sputtered and layered (S-free) precursor films were also annealed using conditions similar to those described previously. This approach is similar to the thin-film synthesis of
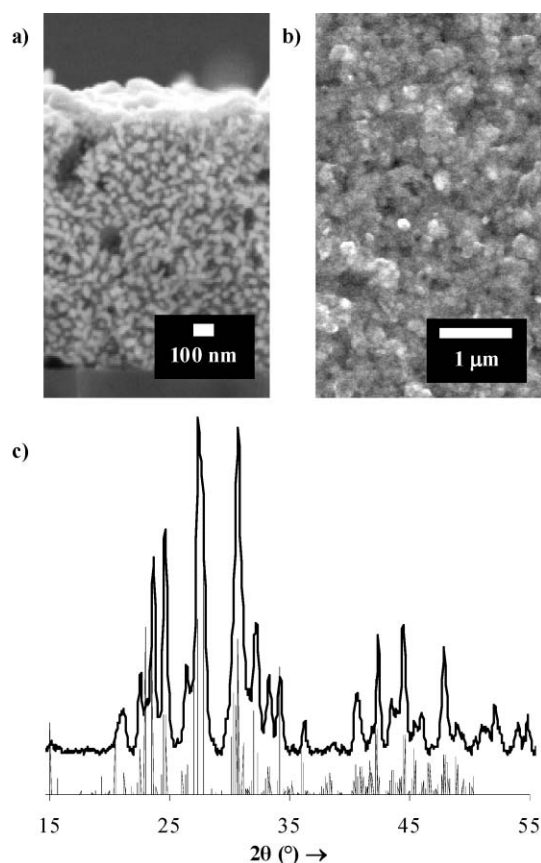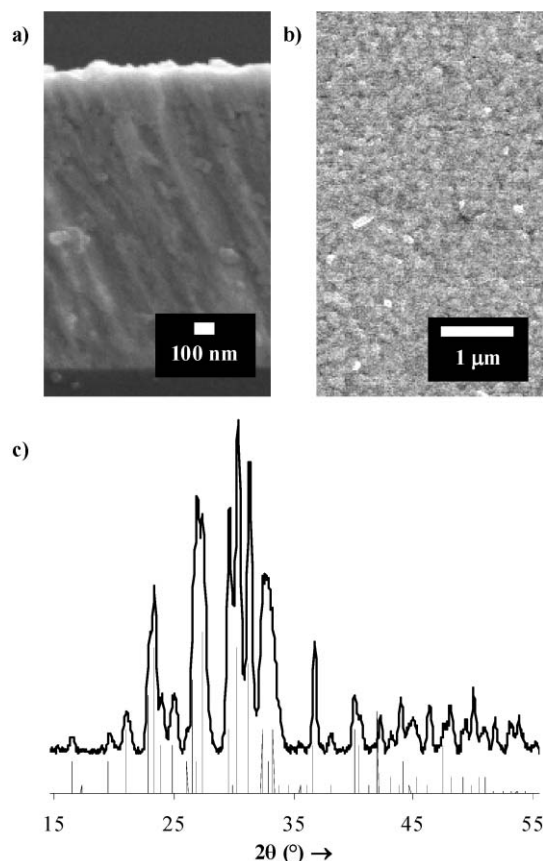

Fig. 3 Semseyite ($Pb_9Sb_8S_{21}$) film. a) Cross-section SEM image, b) top surface SEM image and c) XRD pattern and semseyite reference pattern.[2]

$CuIn(Se,S)_2$[12,13] from chalcogenization of Cu–In metallic precursors. In contrast with the sulfur-containing layered precursor films, the metal precursor films yielded rough films with poor morphology. Moreover, they rarely produced phase-pure films. Films annealed at 375 °C for up to 3 h contained a mixture of a binary phase and a ternary phase, and films annealed at 400 °C for 1 h contained a mixture of one of the plagionite group phases and one of the low temperature phases of the Pb–Sb–S phase diagram evaluated using "dry" solid state syntheses.[14] WDX data on as-deposited and annealed films showed that metal precursor films, unlike sulfur containing layered precursor films, usually suffered significant Sb depletion during annealing. Thus, the incorporation of sulfur into the precursor film is critical for obtaining ternary phase-pure films without significant depletion of Sb. The growth of phase-pure films with good morphology was possible because the Sb : Pb ratio was preserved and shorter annealing times were required.

Short duration reactive annealing of layered precursor films exclusively yielded plagionite group phases, indicating that plagionite group phases easily nucleate under the annealing conditions used. As our growth method cannot enable hydrogen incorporation into the films, it is very unlikely that the plagionite group phase occurrence depends on the presence of hydrogen, as hypothesized by Garvin.[1] Also, a review of the crystallographic density shows that these phases are slightly less dense than the low temperature phases[14,15] boulangerite, robinsonite and zinkenite, and that they are denser than the higher temperature phases that

Fig. 2 Plagionite ($Pb_5Sb_8S_{17}$) film. a) Cross-section SEM image, b) top surface SEM image and c) XRD pattern and plagionite reference pattern.[3]

have been reported. As plagionite group phases failed to appear in the Pb–Sb–S phase diagram established from traditional solid state reactions,[14] their low density as well as several experimental observations described hereafter suggests that they may be metastable phases.

Annealing of plagionite group compound thin films at 400 °C under 1 atm of Ar for 12 h induced decomposition to a mixture of phases including PbS along with loss of Sb_2S_3. Neither plagionite nor semseyite was stable at 400 °C for long periods, confirming previous reports.[1,6] Furthermore, Robinson produced semseyite, plagionite, and fülöppite from aqueous solutions at temperatures between 340 °C and 435 °C,[6] whereas Garvin investigated the phase diagram to temperatures as low as 300 °C using dry synthesis, and KCl–LiCl and NH_4Cl–LiCl fluxes and obtained none of the plagionite group phases.[1] Perhaps significantly, Garvin's reactions were all maintained at temperature for at least 7 days and then quenched, while Robinson's reactions were maintained at the maximum temperature for at most 24 hours and then slowly cooled to room temperature over 2–10 days, enabling successive phases to deposit in layers during slow cooling.[6]

Taken collectively with our results, it appears that formation of the plagionite phases requires short reaction times at temperatures below 435 °C, enabled in our case by intimate mixing of the Pb, Sb, and S in the precursor films. The plagionite group phases are also relatively scarce in nature.[1] All these observations suggest that plagionite phases are likely to be metastable. Indeed, our novel thin-film approach to synthesize lead antimony sulfides may favor the synthesis of metastable phases, as moderate annealing temperatures and durations are required to interdiffuse reactants that are in close proximity, similar to other thin film syntheses producing metastable phases.[16]

Sulfurization of the unique crystalline PbS and amorphous (Sb,S) layered precursor films yields smooth, continuous and phase-pure films of $Pb_5Sb_8S_{17}$ (plagionite) and $Pb_9Sb_8S_{21}$ (semseyite). Synthesis of the other plagionite group phases and characterization of optical properties of the films will be published elesewhere. Several experimental observations suggest that the plagionite phases are likely to be metastable phases. Moreover, films of the plagionite group phases were preferentially obtained with our thin-film growth process, indicating that the presence of hydrogen is not necessary for their occurrence.

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