

Growth characteristics of tin sulphides crystals by the vapour transport method using SnS and sulphur powders: effect of temperature and pressure

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Tin sulphide compounds have two different types of 2D layered crystal structures with different electrical conduction types. Tin disulphide with n-type semiconductor characteristics has a 2D crystal structure with hexagonal symmetry, while tin monosulphide (SnS) with p-type semiconductor characteristics has a 2D crystal structure with orthorhombic symmetry. These layered materials have many potential applications such as electronic and optoelectronic devices. Meanwhile, it is known that the growth products of tin sulphides are very sensitive to the process parameters. In this study, the authors investigated the growth phenomena of tin sulphides by the vapour transport method using SnS and sulphur powders because vapour transport reactions are relatively simple and facilitate the understanding of the effects of growth parameters. The growth behaviour of tin sulphides as a function of process temperature and pressure was observed, and the results can be explained in terms of the sulphurisation and reduction of SnS powder during the growth process.

1. Introduction: Among the various kinds of 2D layered materials with semiconductor characteristics, tin sulphides are especially interesting because these materials have two different types of layered crystal structures with different electrical conduction types [1, 2]. Tin disulphide (SnS₂) and tin monosulphide (SnS) have 2D layered crystal structures with hexagonal symmetry (space group = *P-3m1*) and orthorhombic symmetry (space group = *Pnma*), respectively. Moreover, tin sulphides have many interesting physical properties and are readily applicable to semiconductor-based devices. SnS₂ exhibits n-type semiconductor properties with a relatively large band gap of 2.18–2.77 eV [1, 3], which means that it could be used as an electronic device [4], photoelectric device [5, 6], or chemical sensor [7]. SnS exhibits p-type semiconductor characteristics having high photo-sensitivity and a high absorption coefficient, which could make it useful in photoelectric applications [8, 9]. Moreover, this implies the possibility of implementing 2D heterojunction devices based on n-type SnS₂/p-type SnS; and hence composed of the same chemical elements [1, 3]. Tin sulphides have been synthesised using various methods, such as pyrolysis [3, 10], chemical vapour deposition [1, 11–13], and atomic layer deposition [14, 15]. Meanwhile, the growth products and specific tin sulphides formed are susceptible functions of the process parameters, such as temperature and pressure, within the process window. Therefore, for the selective synthesis of SnS₂ and SnS, it is essential to understand and control the factors that determine the synthesis products. In previously reported studies, phase-controlled synthesis of SnS₂ and SnS crystals using SnO₂ and sulphur powders was demonstrated by controlling the growth ambient or temperature [1, 16]. This process, based on chemical vapour deposition, requires consideration of the chemical reactions between the metal oxide and the sulphur powder.

In the present study, therefore, we investigated the growth phenomena of tin sulphide compounds by the vapour transport method using SnS and sulphur powders, because the vapour transport reaction is relatively simple and facilitates an understanding of the effects of growth parameters. The variation of growth products was investigated as a function of the process conditions of temperature and pressure, and the synthesis route of the growth products was analysed on the basis of sulphurisation and reduction reactions of SnS powder during the growth process.

2. Experimental section: The tin sulphides, either hexagonal SnS₂ or orthorhombic SnS, were synthesised on silicon dioxide (SiO₂)/Si substrates (SiO₂ = 300 nm) by the vapour transport method in a single-zone quartz tube furnace using SnS and sulphur powders. As shown in Fig. 1a, the SnS and sulphur powders were placed in separate alumina boats that were located in the centre of the heating zone and in the lower temperature zone upstream, respectively. The SiO₂/Si substrate was positioned downstream of the heating zone, and its temperature was maintained about 50°C lower than the temperature in the heating zone during crystal growth. Before the synthesis process, the furnace was evacuated to 10⁻³ Torr and purged by a 100 sccm flow of N₂ for 10 min. Then, an inert environment was established by flowing N₂ gas at 20 sccm. As shown in Fig. 1b, the furnace temperature was gradually increased for 20 min until the temperature of the SnS powder reached 500–700°C; this temperature was maintained for an additional 20 min to implement the synthesis. After that, the furnace was cooled down for 30 min at a cooling rate of 10°C/min and was then rapidly cooled to room temperature. During the entire process, the chamber pressure was maintained at 1 Torr (designated as ‘low pressure (LP)’) or at 760 Torr (designated as ‘atmospheric pressure (AP)’) by using a valve between the chamber and the vacuum pump while maintaining a constant flow of 20 sccm of N₂. The synthesised crystals were characterised by optical microscopy (OM; SAMWON Inc., KSM-BA3) and by micro-Raman spectroscopy (UniNanoTech Co. Ltd, UniDRON) with a 532 nm laser. The morphological characteristics were confirmed using field-emission SEM (Tescan, MIRA-3), and the crystal phases of the powder precursors were examined by XRD (RIGAKU, D/MAX-2500) in 2θ scan mode using Cu Kα radiation (λ = 1.5405 Å).

3. Results and discussion: Fig. 2a shows a set of OM images of the samples that examine the growth trends resulting from the variation of the synthesis temperature and pressure. To facilitate clear and succinct comparison, the temperature was set at intervals of 50°C between 500 and 700°C with two pressures of AP (760 Torr) and LP (1 Torr), respectively; and we confirmed that the appearances of the growth products clearly changed in response to the process conditions of temperature and pressure. In the case of AP in the first row of Fig. 2a, there was no significant change in the

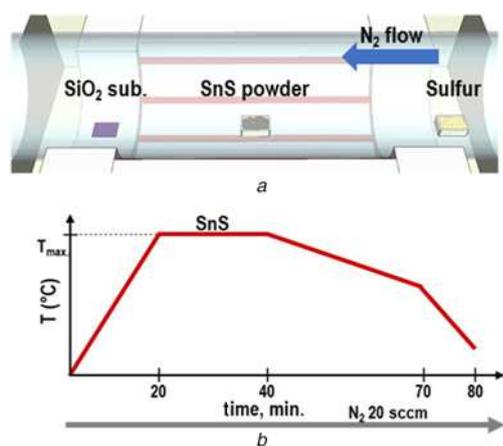


Fig. 1 Experimental conditions

a Schematics

b Growth temperature profile for the synthesis of SnS or SnS₂ crystals by the vapour transport method using SnS and S powders

substrate with increasing temperature up to 550°C; and then the amber-coloured materials were observed at 600–700°C. Meanwhile, in the case of LP (the second row), the colours of the synthesised products changed dramatically with increasing growth temperature. The substrates were covered by amber-coloured materials at 500 and 550°C, while black-grey-coloured material can be seen at 650°C; moreover, at 700°C, the substrate appears to be completely bare, because the boiling point is dropped to about 1000 K at 1 Torr. In particular, at 600°C, a black-to-amber gradual colour change can be observed from the inlet to the outlet side on a single substrate.

To characterise the synthesised crystals, Raman spectroscopy was performed on the amber-coloured sample synthesised at LP (550°C) and the black-grey-coloured sample synthesised at LP (650°C). As shown in Figs. 2b and c, the Raman spectra obtained from the amber-coloured sample and the black-grey-coloured sample both corresponded closely with previously reported Raman peaks of SnS₂ ($A_{1g}=314\text{ cm}^{-1}$, $E_g=205\text{ cm}^{-1}$) and of SnS ($A_g=109$ and 260 cm^{-1} , $B_{2g}=77, 170,$ and 182 cm^{-1}) [1], respectively. These simple observations provide some clues to identify trends in the synthesis of tin sulphide crystals, i.e. the phase of the grown tin sulphide compounds transforms from SnS₂ to SnS as the temperature increases, and the growth temperature for SnS₂ shifts to lower temperatures as the pressure decreases. In fact, this synthesis phenomenon for tin sulphides can be explained by the previously reported thermodynamics of the S–Sn system. According to Lindwall *et al.*, the thermodynamically stable phase in the sulphur-rich region of the S–Sn system changes with increasing temperature from SnS₂ to Sn₂S₃ at about 570°C, and then to SnS at about 670°C at a pressure of 1 mbar [17]. Although the Sn₂S₃ phase was not observed in our case because the compositional ratio of S/Sn was not fixed (caused by our use of an open system), this thermodynamic result is in good agreement with the result of the phase change from SnS₂ to SnS in a similar temperature range at 1 Torr. Moreover, it can also be seen from the results of the thermodynamic simulation that the process condition where SnS₂ is stable in the AP is shifted to a higher temperature than the LP condition.

It is especially interesting that a black-to-amber graded coloured region was observed at LP (600°C), which was in the mid-process window range for the transition between amber-coloured SnS₂ and the black-grey-coloured SnS phase. In fact, as shown in Figs. 3a and b, it was confirmed by the Raman data that the regions with the black-grey-colour on the upstream side of the sample and with the amber-colour on the down-stream side of the same sample were the SnS and SnS₂ phases, respectively.

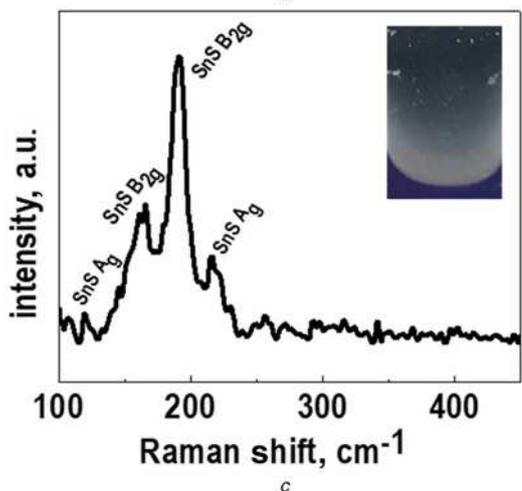
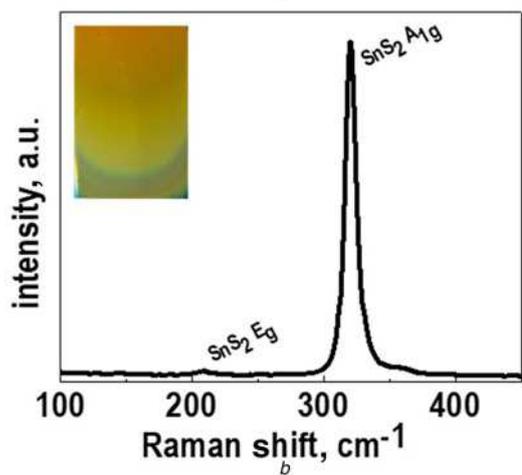
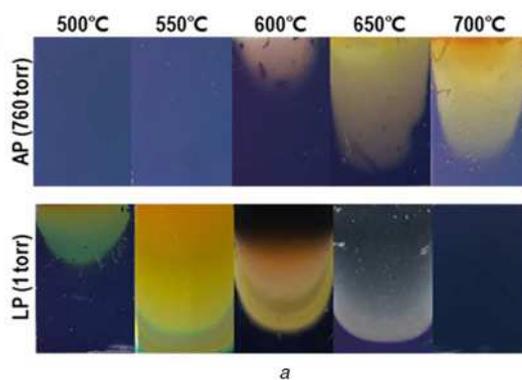


Fig. 2 Growth trends resulting from variation of the synthesis temperature and pressure

a OM images of the samples

b, c Raman spectra obtained from samples synthesised at LP (550 and 650°C), respectively

Moreover, the cross-sectional SEM analysis in Fig. 3c shows that the black-grey-coloured region was vertically composed of two distinct layers, and each layer had a different morphology: The lower layer looks like tightly packed flakes and the upper layer looks as if saddle upon it. By exfoliating the upper layer using vacuum tape, it was confirmed that amber-coloured crystals exist in the lower layer, and this was confirmed to be SnS₂. Through this observation, it is understood that at the beginning of the synthesis process, the amber-coloured SnS₂ layer was formed throughout the substrate, and then the SnS layer was formed in restricted regions upstream during the same process. In other words, this means that the SnS/SnS₂ bi-layer structure can be formed in a suitable process range

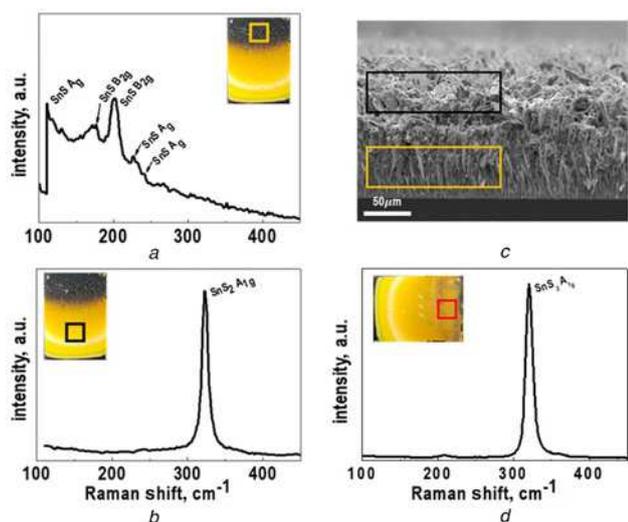


Fig. 3 Analysis for a sample synthesised at LP; 600°C
a, b Raman spectra obtained from the regions marked in the inset figures
c Cross-sectional SEM images for the black–grey-coloured region
d Raman spectrum obtained after peeling away the upper layer of the black–grey-coloured region

in which SnS₂ and SnS can be synthesised. However, in the case of AP (700°C), it shows only amber colour SnS₂ without SnS. The reason for this result in the AP state is that the stable phase of the system cannot be the SnS unless the ratio of S falls below 0.5. Moreover, the reduction of SnS₂ to SnS is impossible since the decomposition reaction of SnS₂ to SnS and S has positive Gibbs-free energy at AP, and SnS₂ phase is stable up to 735°C [18].

To understand these growth phenomena, XRD analysis was conducted on three powder samples: plain unprocessed SnS powder [Fig. 4a-I]; the powder remaining after processing at LP 550°C [Fig. 4a-II]; and the powder remaining after processing at LP 600°C [Fig. 4a-III]. As shown in Fig. 4b, the SnS powder was sulphurised to SnS₂ during the processing at LP (550°C), while the SnS powder exhibited the mixed phases of SnS and SnS₂ after processing at LP (600°C). These results indicate that SnS powder was sulphurised to SnS₂ at relatively low process temperatures (about up to 550°C), and then the sulphurised powders started to revert to the SnS phase by a reduction process at higher temperatures (about 600°C). Therefore, SnS₂ crystals could be formed using SnS and sulphur powders at LP (550°C) because the sulphurised powder was vapourised and recrystallised on the substrate located in the lower temperature region. However, at higher temperatures of 600°C or above, it is thought that SnS crystals were formed rather than SnS₂ crystals because the sulphurised powder was reduced to the SnS phase again. Figs. 4c and d show the SEM images and growth morphology as functions of the growth time during LP (600°C), demonstrating the growth evolution of the SnS₂/SnS bi-layer structure. It can be seen that when the temperature of the furnace was raised to 600°C, SnS₂ crystals with the form of hexagonal plates were laterally formed, and then SnS crystals were formed in the vertical direction at the growth temperature of 600°C. The reason why SnS₂ crystals were formed at this stage rather than SnS crystals is thought to be that the sulphurised powder to the SnS₂ phase was not sufficiently reduced to SnS during the time that the temperature was rising. However, as the processing time continued at 600°C, the sulphurised powder was reduced to SnS; thus, additional SnS crystals were synthesised on the initially grown SnS₂ crystals. We believe that the SnS₂/SnS bi-layer was formed as a result of this process. Moreover, it was found that the phase change of the SnS powder by the sulphurisation and reduction processes was a significant factor in determining

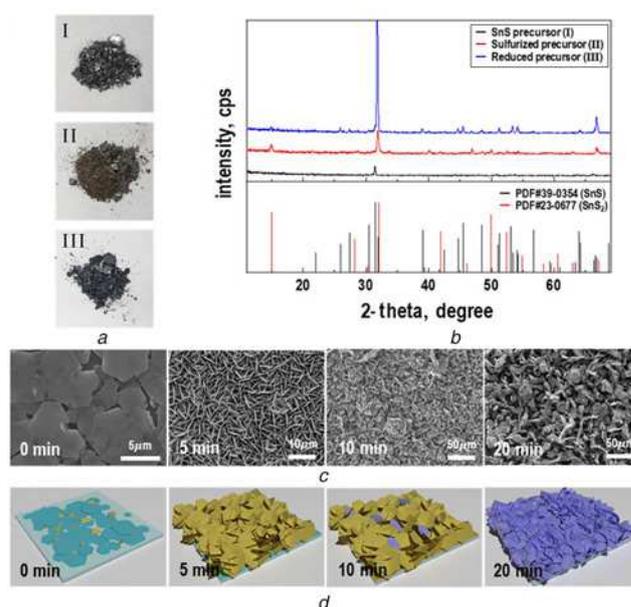


Fig. 4 Growth model
a OM images: (I) plain unprocessed SnS power; (II) SnS power remaining after processing at LP (550°C); (III) SnS power remaining after processing at LP (600°C)
b XRD data of SnS powder before and after processing at LP (550 and 600°C)
c SEM images
d Growth morphologies as a function of the growth time during LP (600°C) processing

the growth phenomena of tin sulphides by the vapour transport method.

4. Conclusion: We investigated the growth phenomena of tin sulphides by the vapour transport method using SnS and sulphur powders. It was observed that the phase of grown tin sulphides transforms from SnS₂ to SnS as the temperature increases, and the growth temperature for SnS₂ shifts to lower temperatures as the pressure decreases. By analysing the powders after reaction and by investigating the growth evolution over time, the change of growth phenomena could be explained by the phase changes of the SnS powder according to the growth conditions.

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